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Microbiological and Organic Studies in Reclaimed Coal Mine Backfill at a Mountain and a Prairie Minesite in Alberta

L-81

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MICROBIOLOGICAL AND ORGANIC GEOCHEMICAL STUDIES IN RECLAIMED COAL MINE BACKFILL AT A MOUNTAIN AND A PRAIRIE MINESITE IN ALBERTA

by

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for

RESEARCH MANAGEMENT DIVISION
Alberta Environment

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March 1983

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TABLE OF CONTENTS

		Page
LIST OF TABLES		viii
LIST OF FIGURES		x
EXECUTIVE SUMMARY		xiii
1.	INTRODUCTION	1
1.1	The Problem	1
1.1.1	Background	1
1.1.2	Objectives	2
1.2	Description of Study Sites	3
1.2.1	Whitewood Mine	3
1.2.1.1	General Setting and Climate	3
1.2.1.2	Soils and Vegetation	5
1.2.1.3	Geology	5
1.2.1.4	Instrumentation	6
1.2.1.5	Hydrology	7
1.2.1.6	Groundwater Inorganic Chemistry	10
1.2.2	Canmore Mine	18
1.2.2.1	General Setting and Climate	18
1.2.2.2	Soils and Vegetation	20
1.2.2.3	Geology	21
1.2.2.4	Instrumentation	24
1.2.2.5	Hydrology	24
1.2.2.6	Groundwater Inorganic Chemistry	31
1.3	Literature Review	33
1.3.1	Organic Compounds Leached from Coal by Aqueous Solution	33
2.	ORGANIC GEOCHEMISTRY	39
2.1	Methodology	39
2.1.1	Field Sampling	39
2.1.1.1	Preliminary Geochemistry	39
2.1.1.2	Storage Experiments	46
2.1.2	Choice of Organic Analyses	54
2.1.3	Organic Analytical Methodology	55
2.1.3.1	Tannins and Lignins	56
2.1.3.2	Carbohydrates	56
2.1.3.3	Phenols	56
2.1.3.4	Dissolved Organic Carbon	57

continued ...

TABLE OF CONTENTS (CONTINUED)

		Page
2.1.3.5	Humic and Fulvic Acids	57
2.1.3.6	Amino Acids	58
2.2	Results of Field Sampling	60
2.2.1	Canmore - General Results	60
2.2.1.1	Tannins and Lignins	60
2.2.1.2	Carbohydrates	67
2.2.1.3	Humic Acids	67
2.2.1.4	Fulvic Acids	68
2.2.1.5	Dissolved Organic Matter	68
2.2.1.6	Phenols	68
2.2.1.7	Amino Acids	69
2.2.2	Organic Chemical Changes Through a Cross-Section at Canmore	79
2.2.3	Wabamun - General Results	86
2.2.4	Relations Between Organic Parameters and Depths Inside and Outside the Wabamun Mine	87
2.2.5	Changes in Organic Parameters Over Time Inside and Outside the Wabamun Mine	105
2.2.6	Changes in the Concentrations of Organic Parameters Over a Cross-Section of Wells and Piezometers at Wabamun	121
2.2.7	Amino Acids at Wabamun	129
2.3	The Influence of Revert Upon Organic and Inorganic Groundwater Chemistry	135
2.4	Discussion	144
3.	MICROBIOLOGICAL INVESTIGATIONS RELATED TO COAL MINING	149
3.1	Introduction	149
3.1.1	Heterotrophic Bacteria	149
3.1.2	Autotrophic Bacteria	152
3.1.2.1	Iron Bacteria	152
3.1.2.2	Sulphur Bacteria	155
3.2	Methods of Microbiological Sample Collection and Analysis	159
3.2.1	Direct Counts Using Epi-flourescence	159
3.2.2	Plate Counts	159
3.2.3	Sulphate Reducers	160
3.2.4	Iron Oxidizers	160
3.3	Results	161
3.3.1	Direct Counts and Plate Counts	161
3.3.2	Sulphur Reducing Bacteria	163
3.4	Discussion	165

continued ...

TABLE OF CONTENTS (CONCLUDED)

		Page
4.	LEACHING OF COAL AND SPOIL MATERIAL IN THE LABORATORY	169
4.1	Introduction	169
4.1.1	Methodology	169
4.2	Results - The Organic Chemistry of Coal	173
4.2.1	Sterile Experiments	173
4.2.2	Non-Sterile Experiments	177
4.3	The Leaching of Uncontaminated Overburden	177
4.4	Influence of Varying Amounts of Coal in Overburden Material on the Chemistry of Leachates	186
4.5	The Influence of Revert Upon the Chemistry of Leachates	189
4.6	Discussion	190
5.	SYNTHESIS	192
6.	REFERENCES CITED	199

LIST OF TABLES

		Page
1.	Water chemistry at the Whitewood Mine, after Anon. (1979)	11
2.	Water chemistry outside the Whitewood Mine, after Anon. (1979)	12
3.	Trace elements inside and outside the Whitewood Mine, after Anon. (1979)	14
4.	Average water chemistry in wells within the Whitewood Mine, after Anon. (1979)	15
5.	Average water chemistry in piezometers within the Whitewood Mine, after Anon. (1979)	16
6.	Groundwater chemistry comparisons	17
7.	Description and carbonate content of representative samples of spoil from Canmore Reclamation Site 2	22
8.	Extractable cations and cation exchange capacity from samples of spoil taken from Canmore	23
9.	Hydraulic head measurements in Canmore piezometers	26
10.	Oxygen-18 measurements from Canmore groundwaters	28
11.	Hydraulic conductivity and transmissivity of Canmore piezometers	30
12.	Metal analysis fron Canmore Creek, mine effluent, and piezometers	32
13.	Organic compounds found in groundwater by Campbell, Pellizzari, and Santor (1978)	35
14.	The concentration of toxic organic compounds in coal leachates found by Wachter and Blackwood (1978)	36
15.	Summary of environmental behaviour of classes of organic coal conversion effluent constituents	38
16.	Geochemical data collected at Wabamun	45
17.	Tests of relationships between all combinations of parameters measured at Canmore using linear regression analysis	61
18.	Tests of relationships between various parameters and depth at Canmore using linear regression analysis	62

LIST OF TABLES (CONCLUDED)

		Page
19.	Average values found at Canmore for all organic parameters measured	63
20.	Identifications of amino acids by number which correspond to the x-axis of the graphs in Figures 12 and 13	70
21.	Changes in the concentrations of organic parameters on a seasonal basis as groundwater passes through spoil material from the forest edge at Canmore	80
22.	Summary of changes in concentration of organic parameters over time at Control Site 2, Site 1, and Site 4 at Wabamun	106
23.	Comparison of average chemistry of groundwater sampled from wells and piezometers affected by Revert and those augered installations which were not	137
24.	Abbreviated bibliography of papers dealing with the uptake of natural organic matter in ground and surface waters	153
25.	The environmental requirements and reactions catalyzed by several common sulphur bacteria in soil	157
26.	Geologic materials used in leaching experiments	172
27.	Summary of total amount leached for leaching experiments 0 to 4	174
28.	Statistical correlations between different parameters in the Wabamun overburden leaching experiment (#9)	182
29.	Summary of total amount leached for leaching experiments 5 to 9	183

LIST OF FIGURES

		Page
1.	Situation map of the Whitewood Mine; Wabamun, Alberta	4
2.	Situation map of Reclamation Site 2; Canmore, Alberta	19
3.	Cross-section through Reclamation Site 2 showing lithology	25
4.	Geochemical data collected at Canmore	42
5.	First storage experiment	48
6.	Second storage experiment	50
7.	Third storage experiment	52
8.	Fourth storage experiment	53
9.	Concentrations of organic parameters measured over time at Canmore in Piezometer 1	64
10.	Concentrations of organic parameters measured over time at Canmore in Piezometers 3	65
11.	Concentrations of organic parameters measured over time at Canmore in the tributary to Canmore Creek which drains the spoil bank	66
12.	Concentrations of amino acids found at selected sampling sites at Canmore on April 30, 1979	71
13.	Concentrations of amino acids found at all sampling sites on 1979 July 17 at Canmore	73
14.	Tannins and lignins sampled from installations in a cross-section through the Canmore Mine Reclamation Site 2	81
15.	Carbohydrates sampled from installations in a cross-section through the Canmore Mine Reclamation Site 2 .	82
16.	Humic acids sampled from installations in a cross section through the Canmore Reclamation Site 2 . . .	83
17.	Fulvic acids sampled from installations in a cross-section through the Canmore Reclamation Site 2 . . .	84

LIST OF FIGURES (CONTINUED)

		Page
18.	Dissolved organic matter from installations in a cross-section through the Canmore Reclamation Site 2	85
19.	Relations between organic parameters and depth inside and outside the Wabamun Mine, 1978 Dec. 05	88
20.	Relations between organic parameters and depth inside and outside the Wabamun mine, 1979 March 22	91
21.	Relations between organic parameters and depth inside and outside the Wabamun mine, 1979 June 06	94
22.	Relations between organic parameters and depth inside and outside the Wabamun mine, 1979 Aug. 29	97
23.	Relations between organic parameters and depth inside and outside the Wabamun mine, 1979 Nov. 14	101
24.	The concentration of organic parameters over time at Control Site 2	107
25.	The concentration of organic parameters over time at Control Site 1	113
26.	The concentration of organic parameters over time at Site 4	117
27.	Concentration of organic parameters measured in wells along the cross-section line F to F^1 at Wabamun	122
28.	Concentration of organic parameters measured in mine spoil by the deepest piezometer in each site along the cross-section line F-F^1 at Wabamun	126
29.	Amino acid data from Wabamun from samples taken on 1979 June 06	130
30.	^{13}C contents of organic and inorganic carbon used to test for the oxidation of Revert	140
31.	The effect of Revert upon the cation exchange capacity of bentonite	142
32.	Microbiological data from Canmore	162
33.	Microbiological data from Wabamun	164
34.	Relationships between bacteria in groundwater and dissolved organic compounds at Wabamun	166
35.	Leaching apparatus	170

continued ...

LIST OF FIGURES (CONCLUDED)

		Page
36.	Canmore coal treated with sodium azide; relationships between organic parameters and leaching time	175
37.	Autoclaved Canmore coal; relationships between bacteria and dissolved organic compounds	176
38.	Unsterilized coal from Canmore and Wabamun; relationships between bacterial populations and successive volumes of leachate	178
39.	Wabamun overburden (spoil) material; relationships between various chemical parameters and successive leaching volumes	179
40.	Leaching of overburden; microbiological relationships.	184
41.	Leaching of overburden; inorganic relationships . . .	185
42.	Amounts leached from overburden containing varying amounts of organic matter	187
43.	Effect of coal on inorganic geochemistry of overburden at Wabamun	197

EXECUTIVE SUMMARY

Both the organic chemicals dissolved in unpolluted groundwaters and the organic matter found in coal originate from the decomposition of plant material. The formation of coal and soil organic matter are both affected by water and the aqueous organic chemistry of each are similar. Subterranean coal seams are separated from the soil zone by varying layers of overburden in their natural state but strip mining mixes the two and, because of their chemical similarity, it is difficult to separate the effects of coal and soil organic matter in spoil material. The mixing of overburden with coal fines by dragline operations also serves to inoculate the intervening strata with soil zone bacteria under aerobic conditions. The chemical evolution of groundwaters which re-invade the spoil piles has been shown by this report to be partially dependent upon the effects of bacteria, both heterotrophic and autotrophic, because of the increased mineralization of organic matter in spoil material.

Two coal mine reclamation sites were studied; a prairie operation mining sub-bituminous C coal at Wabamun (Alberta) and a mountain coal mine mining a higher grade of bituminous coal at Canmore (Alberta). Both sites are rich in carbohydrate minerals and silaceous clastic rocks and have similar vegetation cover. Measures of oxygen, pH, Eh, and temperature at both sites did not reveal any major differences. Although the types and relative proportions of dissolved organic material found were the same at both sites, more organic matter in general was present in Wabamun groundwaters. This was shown to be at least partially because of the greater solubility and reactivity of the lower grade of coal at Wabamun.

The concentrations of dissolved organic matter were sometimes, but not always, higher in the spoil material than in the undisturbed overburden or coal seams. Samples taken from deeper installations tended to be lower in concentration with respect to dissolved organic matter when individual sites were considered but no general trend could be observed when all the samples from either

site were used. The path of groundwater movement was clearly identified at both sites and groundwater tended to decrease in concentration as it traversed both reclamation sites. The two most obvious influences on concentration were the length of time organic material was exposed to degradation processes in the ground and the spring melt. The influence of spring meltwaters was not simply that of dilution but appeared to be related to the annual cycle of decomposition in shallow soil horizons as well. Concentrations of dissolved organic compounds were found to vary seasonally in both spoil and undisturbed material but the patterns observed were not perfectly synchronous. Low concentrations were found in the spring or early summer at both sites, but seasonal peaks occurred throughout the year.

The concentration of dissolved organic matter in groundwater was clearly influenced by the presence of bacteria (and hence the time exposed to these populations) but no obvious statistical relationship could be established between them. The reason for this is believed to be the heterogeneous nature of both the bacterial populations and the organic matter which results in varying rates of uptake of organic compounds. Most of the organic matter found in groundwater is refractory in nature, consisting of large molecular weight humic and fulvic acids. These materials can only be broken down slowly under geologic conditions and are subject to many different chemical reactions of the aggregation and polymerization type. As a result, the relationship between bacteria and dissolved organic matter can be described as a dynamic equilibrium characterized by stable concentrations of organic material and slowly fluctuating populations of bacteria. Autotrophic bacteria influence the inorganic chemistry of groundwater mainly through the activities of sulphur and iron bacteria. Depending on the amount of oxygen present, sulphide minerals may be oxidized to sulphate or sulphate may be reduced to hydrogen sulphide or back to mineral sulphides. Evidence for both these activities at both minesites was found.

The effects of increasing amounts of coal in overburden material was investigated by laboratory leaching experiments. The

major effects identified are increases in alkalinity and hardness of groundwater caused by mineralization of organic matter by bacteria. A conceptual model is presented which includes the effects upon the cation exchange capacity of clay.

Four questions were to be addressed by this research. They are listed and answered briefly below:

1. What is the influence of spoil material on the organic chemistry of surface and groundwaters?

The influence of spoil material upon organic chemistry appears to be negligible unless the effects of bacterial mineralization are taken into account. The organic chemistry of groundwaters in spoil material seems to be most strongly related to the amount of coal left behind at these sites and less so to the overburden material itself. Leaching of both these disturbed materials results in a higher concentration of tannins and lignins, carbohydrates, humic and fulvic acids, and dissolved organic matter in general which can in turn be at least partially broken down by bacteria. The magnitude of the concentration increases is small but it is sufficient to influence the inorganic chemistry of groundwater because of the mineralization of organic compounds. This effect is most strongly seen in increases of hardness and alkalinity. There does not seem to be any danger from organic compounds in spoil material with respect to drinking water standards at either site.

2. What is the aqueous organic chemistry of undisturbed coal aquifers?

The organic compounds found in coal aquifers are very similar to those found in natural waters everywhere. The majority of compounds present are humic materials which are of large molecular weight and are resistant to degradation. Carbohydrates, tannins and lignins, and amino acids are all present at low concentrations (less than 1 mg/L). Phenols could not be detected by wet chemical methods although some were undoubtably present at low concentrations. These

conclusions are supported in the literature. In all cases, the concentrations of dissolved organic matter found were less than 10 mg/L.

3. Is there a significant difference in groundwaters found in reclaimed mine sites between the Mountain and Prairie regions?

Yes, and these differences are strongly related to the grade of coal present and the amount of coal left behind in the spoil material. Coal from Canmore was less soluble and reactive than coal from Wabamun and it appears that lower grades of coal are more hydrophilic. The increased amount of soluble organic material is not likely to be harmful by itself but the effects of microbial mineralization will most probably be observed in the inorganic chemistry of the reclaimed material. The organic content of the overburden (exclusive of the soil zone) at both sites was low and not as important as the coal content, but research at the Forestburg site indicates that this may not always be the case. Any study of this nature should include organic material leached from both coal and the mineral portions of the spoil material.

4. What is the effect of Revert on organic water analyses?

Although it was concluded that Revert did not affect the organic chemistry of the wells sampled at Wabamun, this was only because a period of at least one year elapsed between the time of drilling and that of sampling. Data collected by the Groundwater Branch of Alberta Environment show that organic concentrations were unnaturally high (sometimes by as much as two orders of magnitude) in the period immediately following drilling. Only extensive pumping and the passage of time rendered these wells usable for organic studies. Laboratory experiments showed that the inorganic chemistry of groundwater sampled from these wells could also be affected, particularly when bentonite plugs were used to seal the installations. Revert should definitely not be used for organic studies unless extensive well development and lag times between sampling and drilling

are contemplated. If clays are present or bentonite plugs are to be used, similar precautions should be taken for inorganic chemical sampling. In all cases breaking agents such as 'Fastbreak' (manufactured by the Johnson Company) or calcium hypochlorite should be used in the course of well development.

1. INTRODUCTION

1.1 THE PROBLEM

1.1.1 Background

As coal becomes an increasingly important economic resource, mining activities continue to intensify in Western Canada. Prairie coal is well suited to the thermal generation of electricity because of its low sulphur content and relative ease of access. The coal is usually taken out by strip mining methods and burned in a generating station on the minesite. Metallurgical grade mountain coal is also usually strip mined and is shipped to Japan for use in the manufacture of steel. Tunnel mining is practised to some extent in the mountains but strip mines include most of the mining operations in Alberta.

One of the problems associated with the development of coal resources is the degradation of surface and groundwater quality, particularly at strip mine sites. This is often of the greatest importance on the prairies where surface water supplies are short and coal seams may be the best groundwater aquifers in the area. Coal mining companies are now legally responsible for the restoration of water quality or for ensuring local freshwater supplies if their activities have eliminated the previous source. If the coal is removed, the quality and accessibility of groundwater is reduced and land reclamation may be impaired. Surface waters are more abundant in mountainous areas and although the economic problems associated with lowered water quality are less pressing, aesthetic considerations must be taken into account.

The problems experienced with strip mining for coal are usually perceived as being within the realm of inorganic chemistry. It has long been recognized, however, that microbiological and organic chemical factors are influential. Microbiological effects have been studied in the coal mines of the eastern United States as the cause of acid mine drainage but the role of organic chemicals in ground and surface waters has not been considered until this time. Although acidification problems do not generally occur in Alberta because of the low sulphur content of the coal and the alkaline

nature of the soils, organic compounds and microorganisms are present and influence water chemistry. The problem under investigation, therefore, is the relationship between the organic geochemistry, microbiology, and inorganic geochemistry of ground and surface waters associated with strip mining for coal in Alberta.

1.1.2 Objectives

The following objectives were set for this project:

1. To provide qualitative and quantitative organic analyses of ground and surface waters (at Canmore) influenced by coal at two mine and reclamation sites;
2. To undertake measurements of physical and chemical parameters influencing this organic matter in ground and surface waters such as temperature, dissolved oxygen, Eh, pH, and other dissolved gases;
3. To complement the existing groundwater project at the Whitewood Mine site by adding a description of organic matter and the geochemical environment and to compare this knowledge from a prairie coal mining site (Whitewood) to a mountain operation (Canmore);
4. Investigate the fixation of organic compounds, nutrients, and metals in the stream draining the reclamation site;
5. Investigate the uptake of organic matter leached from coal, spoil material, and "Revert" (an organic drilling mud used at the Whitewood Mine) in the laboratory; and
6. Make specific recommendations pertaining to the use of Revert in this type of study.

In addition to these objectives, four questions were to be addressed by this research. They are:

1. What is the influence of spoil material on the organic chemistry of surface and groundwaters?
2. What is the aqueous organic chemistry of undisturbed coal aquifers?
3. Is there a significant difference in groundwaters found in reclaimed mine sites between the mountain and prairie regions?
4. What is the effect of Revert on organic water analyses?

These questions are specifically dealt with in the executive summary and more generally in Chapter 5.

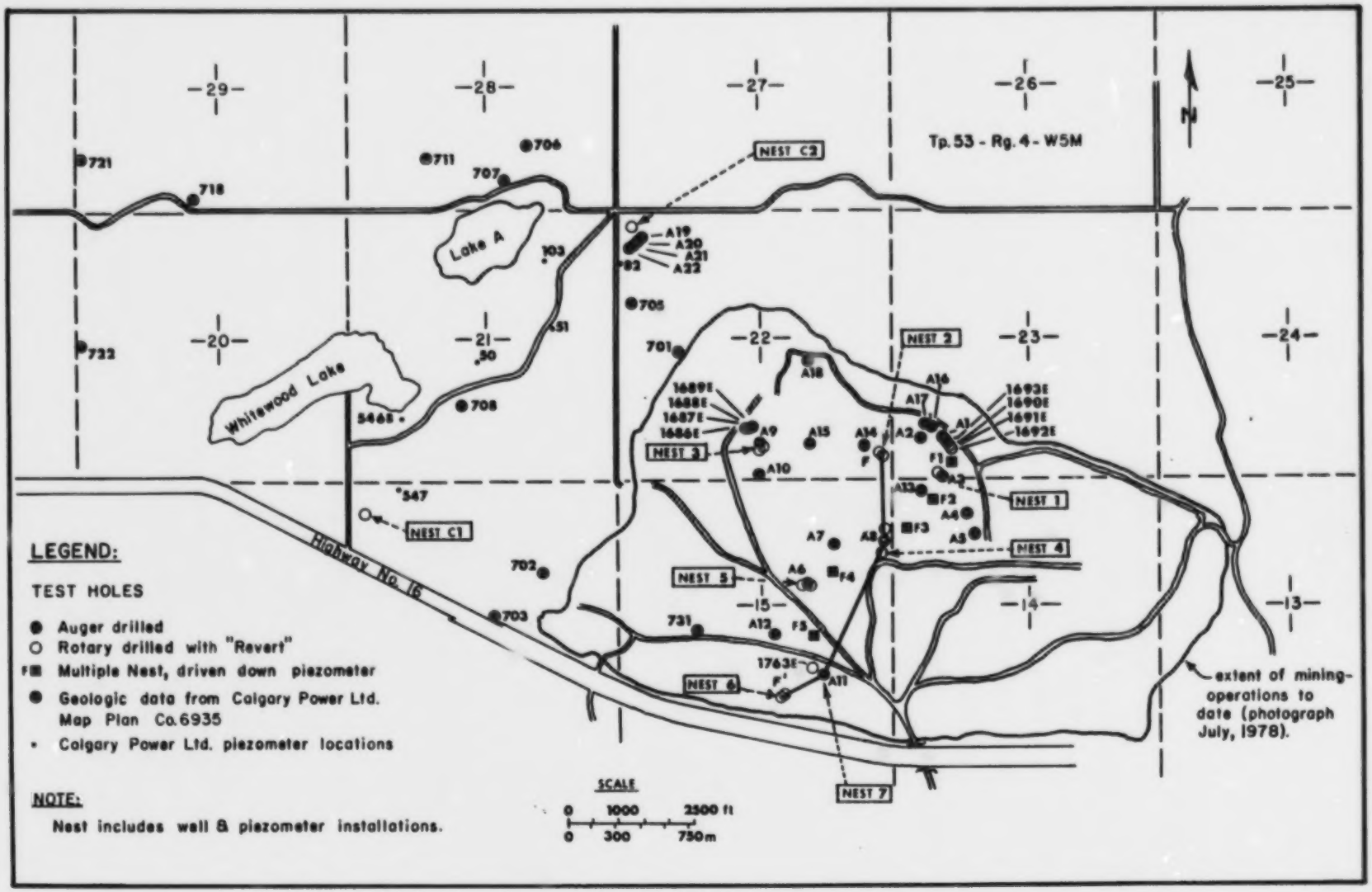
1.2 DESCRIPTION OF STUDY SITES

1.2.1 Whitewood Mine

A detailed description of the Whitewood Mine is presented in the Whitewood Mine Study report (Anon. 1979). For comparative purposes a short synopsis of the description in that report is presented here.

1.2.1.1 General Setting and Climate. The Whitewood Mine (Figure 1) is situated immediately north of the town of Wabumun at a latitude of approximately 53° 36' N and a longitude of 114° 45' W. Located at a mean altitude of 780 m above sea level, the terrain is hummocky with scattered patches of muskeg. The mine site drains towards Lake Wabumun (84.6 km) which rests in Cretaceous bedrock (Schwartz and Gallup 1978). The area experiences a continental climate with an average temperature of 3°C and receives about 500 mm of rain each year. Evapotranspiration accounts for over 90% of precipitation and the number of frost free days ranged from

Figure 1. Situation map of the Whitewood Mine; Wabamun, Alberta.



75 to 90 d/yr. Lake Wabamun is fed almost entirely by groundwater, a significant portion of which drains through the mine site. A power generating station operates on the mine property.

1.2.1.2 Soils and Vegetation. Extensive organic deposits from marshes and bogs are predominant in this area and are the origin of most of the soil groups. Luvisols have developed on till and outwash sands in some areas while some gleysols may be found on lacustrine deposits. Agricultural development has been confined to pasture land on the luvisols which comprise only about 16% of the mining study area. The local vegetation may be classified as being transitory between the Aspen Grove and Mixed Wood sections of the Boreal Forest Zone (Rowe 1972). Upland forest, bog, fen, marshes, and water bodies may be distinguished within this general classification.

1.2.1.3 Geology. Seams of subbituminous coal occur in the Scollard Member which forms the lower portion of the Paskapoo Formation (Cretaceous) at an average depth of 37 m. This member consists mainly of siltstone and coal with intermittent laminae of bentonite. The other member of the Paskapoo Formation, the Upper Paskapoo, is principally composed of sandstone and bentonite. Immediately underneath this formation lies the Edmonton Group with a member tentatively identified as the Whitemud on top and the Horseshoe Canyon Member extending below 150 m. The Paskapoo Formation is overlain by a layer of sand and gravel and glacial till at the surface. The bedrock dips regionally at a rate of 4 to 9 m/km to the southwest. A more detailed discussion of each component of the bedrock and overburden may be found in the Whitewood Mine report (Anon. 1979) as well as maps, lithologic logs, and interpretations.

After mining, the upper surface of the bedrock is highly fractured at or near the contact with the spoil material. Of the original Paskapoo Formation, only 10 to 20 m of the Scollard Member remains after the coal has been removed by the dragline. The spoil material on top of the bedrock is a variable mixture of sand (average 59%), clay (average 24%), silt (average 17%), gravel, and

coal fines (less than 1% together). Compaction of the spoil by machinery and gravity has occurred although the coal fine content is sufficient to prevent excessive compaction in most of the reclaimed area. The amount of gravel in the spoil is low because most of it has been extracted for other purposes during reclamation. The salinity of the spoil material is generally low with Sodium Adsorption Ratios (SAR) of less than 1. The clay minerals present have very little exchangeable sodium but high to very high levels of exchangable calcium and magnesium. The pH ranges from 6.3 to 7.4 but the spoil materials are only mildly calcareous.

1.2.1.4 Instrumentation. As mining activities had commenced many years before this research took place, it was not possible to obtain data from the same overburden before and after mining. For this reason, samples were taken and wells and piezometers installed at sites both inside and outside the mine. Sampling locations outside the mine boundaries were designated as Control Sites and are assumed to be representative of pre-mining conditions. Three Control Sites were established by Groundwater Branch but only Control Site 2 was used for this study, because of analytical limitations and because this site offered the widest range of depths and types of installations.

Wells were installed by Groundwater Branch by rotary drilling to below the base of the spoil material (see Figure 1 for location). Four inch (10 cm) casing (PVC Schedule 40) was cemented in from top to bottom. A PVC screen consisting of three rows of Number 10 slots was used at the bottom of the well. A plug of bentonite was used to ensure that groundwater from above the screen could not pass into the well. The cavity immediately surrounding the screen was filled with commercial 10 to 20 mesh frac. sand. In order to reduce circulation problems a drilling mud known as Revert (Johnson Well Company) was used. Revert is an organic polymer made from the South American Guar bean which is allowed to decompose after the hole has been drilled. The implications of the use of Revert in this study will be discussed in later chapters. The exact drilling procedure may be found in the Whitewood Mine Study report (Anon. 1979).

Piezometers were installed in a manner similar to the wells using Revert, frac. sand, and cement. One piezometer was installed at the first sign of moisture encountered, the second at the base of the spoil pile, and a third at an intermediate position between the two. All wells and piezometers were developed using an air injector for one hour after installation. Although the first series of piezometers was installed using Revert and a rotary rig, a few piezometers were augered in (A16 to A22) so that comparisons might be made between the two methods of installation. Piezometers which penetrate the base of the spoil were installed using both augering and rotary drilling with Revert, as augering alone was not sufficient in bedrock. All wells and piezometers were logged using a variety of techniques and the resulting data may be found in the Whitewood Mine Report.

1.2.1.5 Hydrology. This subject is dealt with at some length in the report of the Whitewood Mine Study (Anon. 1979). A brief synopsis is presented here for comparison with the Canmore site. All field work and interpretation at the Whitewood site were undertaken by personnel of Groundwater Branch but these tasks were also carried out at Canmore within the terms of reference of this project.

The regional groundwater flow is from Lake Isle (northwest of Wabamun) and its environs through the coal and sandstone aquifers of the Paskapoo Formation to Wabamun Lake (Schwartz and Gallup 1978). The direction of flow of deeper groundwater in the vicinity of the Whitewood Mine is not known. Shallower groundwater systems which are influenced by mining activities conform approximately to surface water drainage patterns. Based on information from the Control Sites, bedrock aquifers are semi-confined and are partially connected to the glacial outwash gravel situated immediately above them. This gravel bed varies in thickness from 0 to 6 metres and is overlain by up to 10 m of low permeability till. This till supports a perched water table in regions of lacustrine and organic deposits which may be found in the lowlands between the hummocks on the surface.

The hydraulic properties of all the geologic units down to the remains of the Scollard Member were determined by pump tests on

the wells (analyzed by the Jacob modification of the Theis non-equilibrium formula) and bail tests on the piezometers (analyzed by the Hvorslev method). Every installation was tested on at least one occasion. Hydraulic conductivities and safe yields were calculated whenever possible (Anon. 1979).

The original topography before mining included many marshes and wetlands. After mining and recontouring, a number of enclosed depressions have been created which do not hold water for any appreciable time. The clay content of the surface spoil material restricts infiltration but evapotranspiration rates are high so standing water does not persist. The hydraulic head below these depressions does not show mounding of groundwater so it is possible that evapotranspiration is more important.

Flow nets composed from hydraulic head data show that water moves from the northeast to the southwest. The greatest downward movement of water occurs in the northern portions of the minesite where water is trapped by topographic lows. Toward the southern sections, the flow is almost horizontal. At the southern boundary of the mine, just north of Highway 16 (Figure 1), an area of very high permeability exists. This occurs because old mine workings from the abandoned Victory Mine (which predates the existing Whitewood Mine) included several tunnels which are filled with loose rubble and have become flooded. This region, at the lowest part of the minesite, acts as a conduit for groundwater draining toward the lake. As a result, hydraulic conductivities and well yields are very high in this area.

The two active pits, east and west, are both dewatered during mining operations. This causes depressions in the water table at both ends of the mine which influence the hydraulic head observed in wells and piezometers. Some piezometers no longer penetrate the water table because of this (Nest 3 for example) and it was impossible to calculate aquifer characteristics or to take water samples for analysis from them. When dewatering activities cease, water levels will reach a new equilibrium in the spoil material and bedrock aquifers.

In contrast to lowered water table conditions near the working pits, clay lenses may be found within the spoil material

which have created perched water tables. The best example of this may be seen at Nest 2 where a piezometer has been successfully completed within perched water and samples have been taken. Another perched water table, or perhaps a continuation of the one observed at Nest 2, has been located between Nests 4 and 5. This clay layer may also serve to confine the aquifers located below it to a certain extent.

When well pumping tests were carried out to test the bedrock aquifers, the hydraulic head in adjacent piezometers was also monitored. They were observed not to change, indicating that the pumped aquifers were confined. On other occasions, however, the response of water levels to rainfalls suggested at least some degree of interconnection between the remains of the bedrock aquifers and the spoil material. The hydraulic conductivity in the Bedrock (remains of the Scollard Member) ranges from between 2.3×10^{-1} cm/sec in seams 4 and 5 at Well 6 to 7.1×10^{-4} cm/sec in seam 5 at Well 5. Seam 6 at Control Site 2 has a hydraulic conductivity of 2.5×10^{-3} cm/sec. Two piezometers at Control Site 2, C2C and C2D, had the highest (1.1×10^{-2} cm/sec) and the lowest (4.4×10^{-7} cm/sec) hydraulic conductivities respectively as measured by the Hvorslev method of bail test analysis. All of the others, including the other Control Sites, fell within this range. The hydraulic conductivity was usually found to be higher at the interface between the spoil material and the bedrock. This is thought to be caused by the accumulation of coarse rubble on the floor of the mine pit which becomes buried by less permeable materials as the dragline passes on. Coal seams 4, 5, and 6 have been left in place throughout much of the southern portion of the mine. This occurred because of rapid flooding of the mine pit which made the mine pit floor too soft to support heavy equipment. This may have been caused by the removal of a confining layer of overburden by the dragline and subsequent release of water pressure. At any rate, the coal which is left in place is more permeable than the coal which was removed and the rapid influx of water into the pit suggests that the confining layers between the coal seams have been breached.

1.2.1.6 Groundwater Inorganic Chemistry. Both the Control and the regional wells in the area are dominated by sodium and bicarbonate ions (Tables 1 and 2). Calcium is the second most important cation followed by magnesium and potassium. Sulphate is the only other significant anion in the control and regional wells and only small amounts of chloride are present. The piezo- meters at Control Sites 1, 2, and 3 contain much larger amounts of calcium (calcium is dominant at Control Sites 1 and 2) but their inorganic chemistry is otherwise similar to the control wells. Trace elements are all at low levels in the control wells and piezometers. The trace elements measured were aluminum, antimony, arsenic, beryllium, boron, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc (Table 3). Iron and manganese are present at low levels in the control wells but at much higher levels in some of the control piezometers. The pH of the waters in the control wells and piezometers is typically slightly alkaline, about 7.2.

The mine wells are all dominated by calcium and bicarbonate ions (Tables 4 and 5). Sodium is more abundant than magnesium and potassium and chloride are present only at low levels. Sulphate has taken on a proportionally greater importance but bicarbonate is still the dominant anion. The mine piezometers exhibit the same trend as the mine wells, unlike all of the control installations. Trace elements are at low levels in the mine wells and piezometers although some have increased slightly compared with the controls. Iron and manganese are both much higher in concentration in the piezometers than in the wells. While this could only be described as a trend in the control piezometers (caused by a few high readings), the increase is more consistent within the mine. The increase is more pronounced for iron than for manganese. The pH measured in well and piezometer samples is still slightly alkaline with a few slightly acidic measurements observed. The pH of some of the groundwater sampled is very alkaline, suggesting cement contamination.

The changes in inorganic groundwater chemistry between mine, control, and regional wells and piezometers are summarized in Table 6. Iron increased between mine wells vs. regional wells and mine piezometers vs. regional wells. Calcium, hardness, and

Table 1. Water chemistry (in mg/L) at the Whitewood Mine, after Anon. (1979).

CONTROL WELL AND PIEZOMETER CHEMISTRY AVERAGES

Site No.	Fe	Ca	Hard	K	SO_4	Alk	T.D.S.	Mg	Na	Cl	HCO	Mn
C1	0.75	62	201	3.5	14	345	456	12	68	2	420	0.142
C2	0.19	55	183	10	26	373	497	11	98	2	455	0.111
	0.47	59	192	6.8	20	359	477	12	83	2	438	0.127
σ	0.40	5	13	4.6	9	20	29	1	21	0	25	0.022
±ts n	±0.81	±10	±26	±9.4	±17	±41	±59	±1	±44	±0	±51	±0.045

CONTROL PIEZOMETERS

Piezometer	Fe	Ca	Hard	K	SO_4	Alk	T.D.S.	Mg	Na	Cl	HCO	Mn
C1A	0.42	4	11	45.6	40	67	176	1	20	3	35	0.017
C1B	0.92	92	339	15.1	19	350	465	26	11	4	426	0.252
C1C	0.38	78	307	7.8	10	313	416	29	6	2	391	0.363
C1D	0.55	58	268	5.6	29	287	430	22	27	4	349	1.021
C2A	0.68	97	333	3.5	24	357	461	22	23	4	436	0.305
C2B	0.47	86	302	5.0	26	331	434	21	23	3	404	0.240
C2C	0.18	35	67	18.2	48	133	173	1	37	3		0.009
C2D	7.95	102	387	6.1	24	403	458	32	16	4	535	1.474
C2E	0.72	88	356	7.4	53	525	696	33	90	3	640	0.411
C2F	49.60	80	354	4.2	64	491	655	37	78	4	578	0.199
Median	0.70	87	336	5.9	25	354	463	28	23	4	431	0.335
$\bar{x}$	7.66	85	331	6.8	31	382	502	28	34	4	470	0.533
σ	17.14	14	37	3.7	18	85	109	6	32	1	102	0.462
±ts/ n	±10.08	±8	±22	±2.2	±11	±50	±64	±4	±11	±1	±60	±0.272

Table 2. Water chemistry (in mg/L) outside the Whitewood Mine, after Anon. (1979).

REGIONAL WELLS

Well No.	Fe	Ca	Hard	K	SO	Alk	T.D.S.	Mg	Na	Cl	HCO	Mn
3	0.2	17	49		220	797	1197	1		2	935	
5	1.2	172	369		181	400	678	30		3	489	
11	0.6	134	456		38	347	490	30		64	423	
12	0.1*	158	587		50	304	611	47		158	311	
16	0.1	8	75		155	615	995	14		1	750	
18	0.2	5	17		62	852	993	1*		8	1015	
35	0.4	12	32		25	814	947	1*		42	993	
36	1.1	152	538		75	714	824	38		27	870	
60	0.1	1*	3		33	701	777	1*		7	855	
66	0.01	33	95		90	692	836	0.3		5	40	
94	0.2	142	495		116	346	536	34		16	432	
98	0.05*	85	291		45	444	656	19		2	541	
Median	0.2	51	193		69	658	801	17		12	646	
	0.36	75	267		91	586	791	18		28	643	
σ	0.41	74	244		64	203	203	17		46	304	
± ts/ n	±0.21	±38	±126		±33	±105	±105	±9		±23	±157	

Table 2. Water chemistry (in mg/L) outside the Whitewood Mine, after Anon. (1979) (concluded)

REGIONAL WELLS

Well No.	Fe	Ca	Hard	K	SO	Alk	T.D.S.	Mg	Na	Cl	HCO	Mn
C3	0.24	4	28	101	136	705	1149	4	333	2	550	0.009
C3A	0.89	33	113	4.6	107	425	731	7	196	5	517	0.082
C3B	0.43	78	275	4.4	95	519	795	20	156	2	633	0.259
C3C	1.17	81	330	4.7	54	432	594	31	57	4	516	0.414
C3D	0.72	121	445	4.3	39	468	637	35	29	3	570	1.188
C3E	2.1	126	460	4.2	31	484	643	35	25	3	590	1.948
C3F	0.15	125	444	3.8	52	416	591	31	12	4	508	0.532
C3G	10.61	96	353	4.1	47	391	575	27	44	6	477	1.042
Median	0.18	89	342	4.4	53	476	540	29	51	4	560	0.472
$\bar{x}$	2.04	83	306	4.3	70	479	714	24	107	4	545	0.684
σ	3.51	45	161	0.3	38	100	192	12	113	2	50	0.663
$\pm ts/\sqrt{n}$	±2.31	±29	±106	±0.2	±25	±66	±126	±8	±74	±1	±33	±0.437

* Concentration less than

Table 3. Trace element concentration (in mg/L) inside and outside the Whitewood Mine, after Anon. (1979).

	TRACE ELEMENTS					
	PRE-MINING			POST-MINING		
	RANGE		VALUE*	RANGE		VALUE*
Aluminum	0.020	1.63	0.050	0.020	1.25	0.15
Antimony	0.005		0.0005	0.0005	0.0017	0.0005
Aresnic	0.0002	0.0138	0.0050	0.0002	0.289	0.0050
Beryllium	0.001		0.001	0.001		0.001
Boron	Not done due to low post-mining levels			0.10	0.50	0.20
Cadmium	0.001	0.002	0.0001	0.001	0.009	0.002
Chromium	0.001	0.292	0.005	0.001	0.112	0.005
Copper	0.001	0.054	0.020	0.002	0.150	0.050
Lead	0.003	0.122	0.050	0.003	0.240	0.050
Mercury	Not done due to low post-mining levels			0.0001		0.0001
Nickel	0.001	0.023	0.010	0.001	0.78	0.025
Selenium	0.0002		0.0002	0.0002		0.0002
Silver	0.001		0.001	0.001		0.001
Zinc	0.004	0.134	0.100	0.001	0.680	0.100

* The majority of the results are at or below this level.

Table 4. Average water chemistry (in mg/L) in wells within the Whitewood Mine, after Anon. (1979).[1]

MINE WELLS

Well No.	Fe	Ca	Hard	K	SO_4	Alk	T.D.S.	Mg	Na	Cl	HCO_3	Mn
1	0.31	108	385	12.4	148	414	465	28	77	2	505	0.258
2	0.43	141	455	16.7	137	603	927	25	124	2	735	0.313
3	1.47	140	463	6.6	227	475	893	28	110	2	579	0.258
4	1.93	217	934	9.8	295	605	1216	95	26	4	738	2.460
5	0.62	147	517	4.5	151	465	760	36	48	2	574	0.425
6	0.28	131	460	2.5	67	413	573	32	15	2	504	0.257
7	0.68	122	466	6.4	53	395	556	34	14	8	521	0.380
Median	0.68	140	460	6.6	148	465	760	32	48	2	574	0.313
$\bar{x}$	0.82	144	523	8.4	168	481	801	40	59	3	594	0.622
σ	0.63	35	185	4.9	116	89	233	25	46	3	102	0.797
±ts/ n	±0.45	±25	±133	±3.5	±83	±64	±167	±19	±33	2	±73	±0/572

[1] Concentration values in mg/L except Hard and Alk which are expressed as mg/L $CaCO_3$.

Table 5. Average water chemistry (in mg/L) in piezometers within the Whitewood Mine, after Anon. (1979).[1]

Piezometer	Fe	Ca	Hard	K	SO	Alk	T.D.S.	Mg	Na	Cl	HCO	Mn
1A	0.32	156	584	5.2	172	543	845	42	62	2	647	0.547
1B	0.46	161	580	7.7	173	509	809	45	36	2	600	0.355
1C	18.91	132	512	8.8	181	598	935	41	120	3	728	0.154
2A	0.26	130	460	4.9	117	540	770	32	86	2	652	0.459
2B	1.95	179	799	3.8	118	952	1700	61	174	4	1161	1.940
2C	34.45	174	563	6.5	151	598	909	47	22	2	729	0.890
4A	2.21	177	639	6.4	266	476	947	48	55	2	580	1.005
4B	233.69	281	1064	7.8	37	1136	1356	87	36	7	1385	13.692
4C	9.97	270	1045	3.7	313	842	1383	89	42	3	1026	7.296
5C	3.54	154	529	5.4	137	476	745	40	39	2	630	1.078
6A	58.12	137	460	8.7	149	324	593	29	7	3	437	2.841
6B	43.19	131	424	11.2	108	350	561	23	10	2	428	4.199
6C	2.39	129	465	3.6	61	452	616	35	9	2	551	0.389
7A	0.41	147	537	5.1	65	483	655	41	8	4	589	0.264
7B	0.21	154	603	10.7	157	1005	1416	66	247	15	1225	1.913
7C	0.48	125	456	6.4	26	491	603	36	24	3	598	0.277
Median	2.97	154	550	6.4	143	526	827	42	38	3	639	0.948
$\bar{x}$	26.16	165	607	6.6	139	611	928	48	61	3	748	2.331
σ	58.11	47	300	2.5	77	241	352	18	68	2	291	3.627
$\pm ts/\sqrt{n}$	25.57	21	88	1.1	34	106	155	8	30	1	128	1.596

[1] Concentration values in mg/L except Hard and Alk which are expressed as mg/L $CaCO_3$.

Table 6. Groundwater chemistry comparisons.

CHEMICAL PARAMETER	MINE WELLS VS REG. WELLS	MINE WELLS VS CON. WELLS	MINE PIEZ. VS REG. WELLS	MINE PIEZ. VS CON. PIEZ.
Iron	↑	—	↑	—
Calcium	↑	↑	↑	↑
Hardness	↑	↑	↑	↑
Potassium	o	—	o	—
Sulphate	—	↑	↑	↑
Alkalinity	—	—	—	↑
Total Dissolved Solids	—	↑	—	↑
Magnesium	↑	↑	↑	↑
Sodium	o	—	o	—
Chloride	—	—	↑	—
Bicarbonate	—	↑	—	↑
Manganese	o	—	o	↑

↑ Post Mining is significantly higher at a 90% confidence level.

o Not enough data available for a valid comparison.

— Post Mining is not significantly different at a 90% confidence level after Anon. (1979)- Whitewood Study Report.

magnesium all increased after mining compared with control and regional installations. No net changes were observed in the concentrations of sodium and potassium. Sulphate increased in all comparisons except that between mine piezometers and regional wells. Alkalinity, total dissolved solids, chloride, bicarbonate, and manganese all increased in some cases and not in others. No decreases were observed.

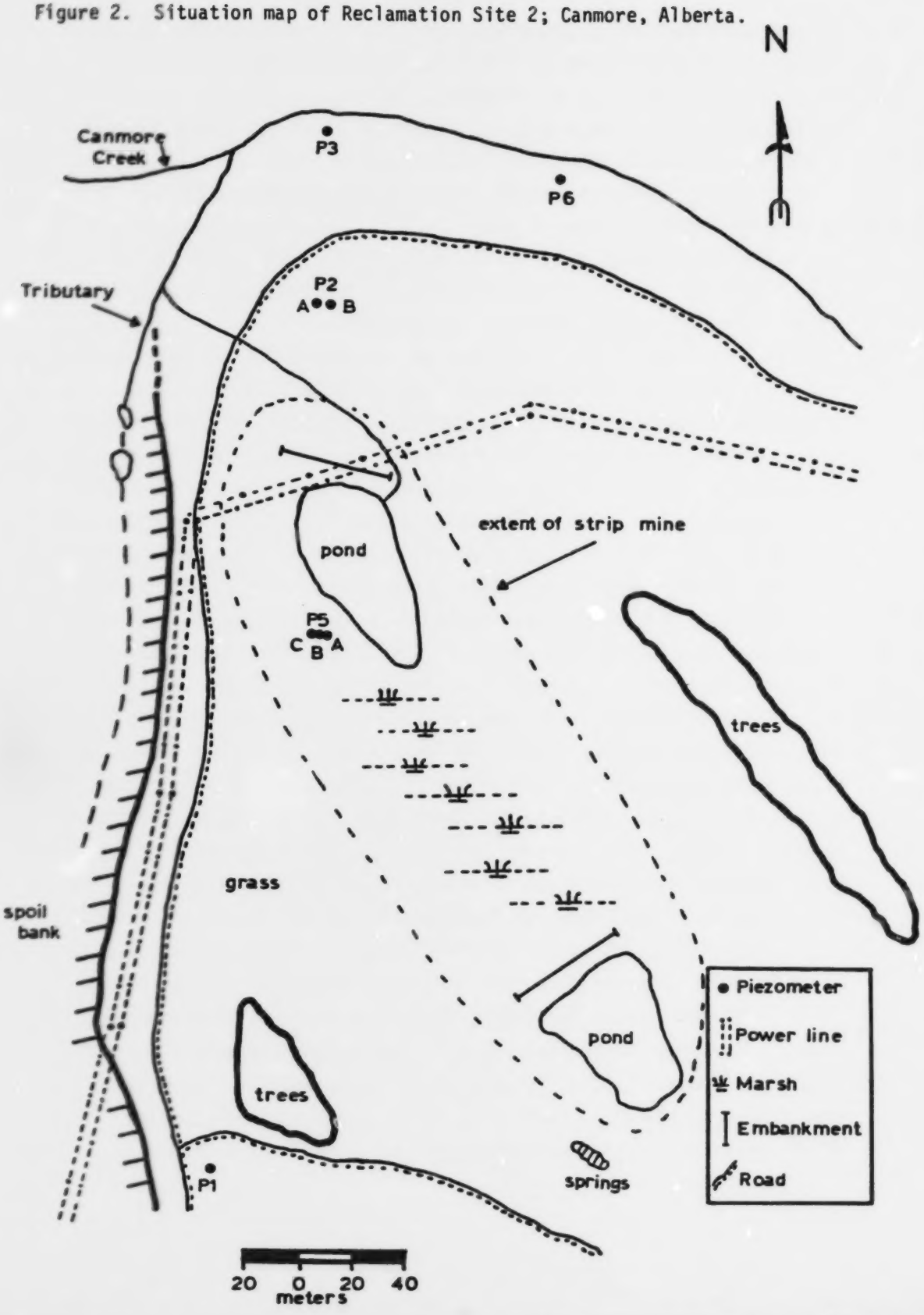
The area around the mine typically exceeds the recommended limits for drinking water (Dept. of National Health and Welfare 1969) with respect to iron, manganese, and alkalinity. This was found to be the case after mining as well with the addition of hardness. These excesses do not represent significant health hazards but do detract from aesthetic expectations and contribute to plumbing problems (formation of scale).

1.2.2 Canmore Mine

The Canmore Mine site did not receive as much attention with respect to the gathering of background information, instrumentation, or experimentation as the Whitewood Mine. While there are no major reclamation problems associated with this site, it should be noted that the scale of operations was very much smaller and the water quality in the area was better to begin with. The site is no longer being worked and has been reclaimed since 1969. It was included in this study for comparison purposes between the two types of coal and geographic settings. Some descriptive background information was collected during this study and other reference sources have been consulted.

1.2.2.1 General Setting and Climate. The Canmore Mine is actually a series of both strip and tunnel operations stretched out over 5 km immediately south of the town of Canmore. It is located at a latitude of 51° 4' N and a longitude of 115° 24' W. This project was carried out at Reclamation Site Number 2 (Figure 2) whose mean altitude above sea level is 1490 m. The site lies at the base of the western arm of the Three Sisters Mountain and the land slopes gently down toward the town of Canmore to the north. The site is drained by a small tributary to Canmore Creek (Figure 2) and

Figure 2. Situation map of Reclamation Site 2; Canmore, Alberta.



several springs feed a marshy area overlying the backfilled overburden directly on top of the old mine. The mine itself covers only 2.5 ha and is flanked on all sides by trees. When the mine was reclaimed, a considerable amount of spoil material was placed around the north and west edges of the old pit, raising the level of the land. The springs are located at the southwest corner of the pit depression and they flow only during the spring and early summer under normal circumstances. By the autumn, the springs, marshy areas, and most of the ponds have dried up. Two embankments have been placed across the width of the depression in order to hold back some of the spring water which flows down overland to Canmore Creek.

The climate is continental with fairly evenly distributed precipitation throughout the year and large fluctuations in temperature. Chinook winds exert a moderating influence in winter but temperatures often dip to -30 ^{o}C. The mean annual precipitation is 595 mm of which 53% falls as snow. The average annual temperature is 2.2 ^{o}C with a frost-free period of about 75 days.

1.2.2.2 Soils and Vegetation. The original soil in the area is made up of brunisols with some regisols and luvisols also present. The soil under the forested portion of the site is thin, high in organic content, and well drained. The backfilled spoil material was reclaimed by hydro-mulching peat from a local swamp into the upper surface and seeding with native grasses. This has resulted in the beginnings of an A horizon and pedogenesis is in progress. Chemical analyses of soils sampled in nearby Bow Valley Provincial Park (Greenlee 1974) show low to medium levels of organic matter, large amounts of potassium, and smaller amounts of sulphate, sodium, calcium carbonate, nitrogen, and phosphorus. Soil pH is mildly acidic under forest soils.

The forest in the area is classified as Sub-alpine by Rowe (1972). This zone is characterized by the Englemann spruce (Picea engelmann) X white spruce (Picea glauca) hybrid complex. Lodgepole pine (Pinus contorta) is locally common as a successional species after forest fires. Alpine fir (Abies lasiocarpa) may be found at

higher elevations and aspen (Populus tremuloides) and balsam poplar (Populus balsamifera) are also common in the area. Various sedges, grasses, and horsetails are also present.

1.2.2.3 Geology. Coal in this region is found in a complex series of folding and thrust faulting in the Kootenay Formation (Lower Cretaceous/Upper Jurassic). The Kootenay Formation consists of a series of interbedded shales, siltstones, and sandstones with minor amounts of coal, ironstone, conglomerate, and cannel. The strata are generally brown to black because of iron oxides and carbonaceous matter (Allan and Carr 1947). The Kootenay Formation outcrops in many places in this region and often contains coal in economically important amounts. It can be anywhere up to 365 m in thickness and is underlain by the Jurassic Fernie Formation. At Strip Mine Number 2 the coal seam has been thrust upwards in a vertical seam very close to the surface so the mine was only 35 m deep at the lowest part of the trough.

The coal in the Kootenay Formation is classified as low-volatile bituminous to semi-anthracite according to the A.S.T.M. classification (Allan and Carr 1947). The coal contains an average of 60% of fixed carbon and is very low in sulphur. The seam in Strip Mine Number 2 has been folded vertically upward so the coal was removed very easily and cleanly by steamshovel and bulldozer. Despite this, a substantial amount of coal ranging in size from fines to cobbles remains mixed in the spoil material.

Analyses of the spoil material are presented in Tables 7 and 8. The amount of calcite present ranges from 25 to 74% and significant amounts of iron are present. Copper, zinc, lead, manganese, nickel, and cadmium are all present in small quantities. The analysis of extractable cations shows a dominance of calcium followed by smaller amounts of magnesium, sodium and potassium. The cation exchange capacity ranges from 1.6 to 16.8 meq/100 g.

Table 7. Description and carbonate content of representative samples of spoil from Canmore Reclamation Site 2.

Sample Number	Depth (m)	Description	%CaCO	%CO -C
1	0.1	Control Piezometer (P1): soil below litter layer - sandy, organic	32.0	3.84
2	1.4	P6: medium to fine gravel, coal fines, sand	26.0	3.12
3	1.1	Control Piezometer (P1): C horizon - sand	48	5.8
4	2.2	Control Piezometer (P1): C horizon - sandy gravel, organic	48	5.8
5	6.8	Control Piezometer (P1): poorly sorted sand and gravel	74	8.9
6	2.5	P5A by pond: medium gravel, sandy, organic coal fines	66	7.9
7	2.6	P2A: sand, fine gravel, coal fines	25	3.0
8	3.3	P2B: clay, sandy loam, coal fines	52	6.2

DPTA extractable metals from representative samples of spoil from Canmore Reclamation Site 2 (in mg/Kg spoil).

Sample Number	Fe	Cu	Zn	Pb	Mn	Ni	Cd
1	66.0	1.0	5.2	0.8	11.0	2.6	.26
2	24.2	2.2	6.6	0.8	2.2	1.6	.28
3	22.0	0.6	0.6	0.2	2.2	1.6	.06
4	35.2	0.8	1.6	0.6	4.4	1.6	.06
5	11.0	0.2	0.4	0.2	2.2	0.2	.02
6	72.6	2.4	8.8	0.4	2.2	3.2	.30
7	41.8	2.0	11.0	0.6	2.2	1.2	.38
8	68.2	2.4	3.6	0.8	8.8	1.2	.06

Table 8. Extractable cations and cation exchange capacity from samples of spoil from Canmore Reclamation Site 2.

Sample Number	K	Na	Ca	Mg	Cation Exchange Capacity
1	1 642	920	71 342	3 890	16.8
2	869	920	60 120	2 674	5.8
3	860	920	69 739	3 403	7.6
4	938	460	68 536	3 403	10.4
5	235	460	49 298	1 459	1.6
6	704	920	61 322	3 160	13.0
7	1 642	920	57 314	4 132	6.4
8	704	1 380	61 322	3 160	4.8

Cation exchange capacity in meq/100g

All other analyses in mg/kg

See TABLE 7 for a description of samples

1.2.2.4 Instrumentation. In September of 1978, eight piezometers were installed in Reclamation Site Number 2 in a transect from the highest point of the site to Canmore Creek (Figure 2). The piezometers were installed using a hollow stem augering rig provided by the Soils Branch of Alberta Environment at Lethbridge. The method of installation was the same as that used at the Whitewood Mine except that no rotary drilling was necessary and no Revert was used. The slotted tips were made with a hacksaw, packed 10-20 mesh frac. sand, and sealed with a bentonite plug. Cuttings were used to backfill the holes. A cross-section through the strip mine including the piezometers is presented in Figure 3, which also shows the lithology reconstructed from the drill logs and information provided by the Canmore Mining Company. In Figure 3, it may be seen that some remnants of coal seams 4 and 5 were left in position as well as other marginal seams. The excavation followed the vertical bedrock face down to the point of poor economic return and was backfilled afterward. The water table has become re-established very close to the surface. Both Canmore Creek and the small tributary which drains the spoil pile were included as regular sampling points with the piezometers as well as some springs when they were flowing in the spring.

1.2.2.5 Hydrology. The large differences in elevation at the Canmore site ensure that the shallow groundwater will be moving from points higher up on the mountain, through the mine reclamation site, and will discharge into Canmore Creek and its tributaries. When the water table is high in the spring, several springs discharge onto the surface of the backfilled material from the remains of the southern cut wall. Groundwater seeps from the base of the spoil pile creating the mine effluent creek which is tributary to Canmore Creek (see Figure 2). At Sites 2 and 5 the additional piezometers permit a measurement of the direction of water movement as water will move from a higher potential to a lower potential. The head measurements (Table 9) at both sites show water movement in both directions at different times of the year but the overall trend is upwards (discharge). One one occasion (July 12, 1979), water appeared to be moving downward at Site 2 but the potential is so

Figure 3. Cross-section through Reclamation Site 2 showing lithology.

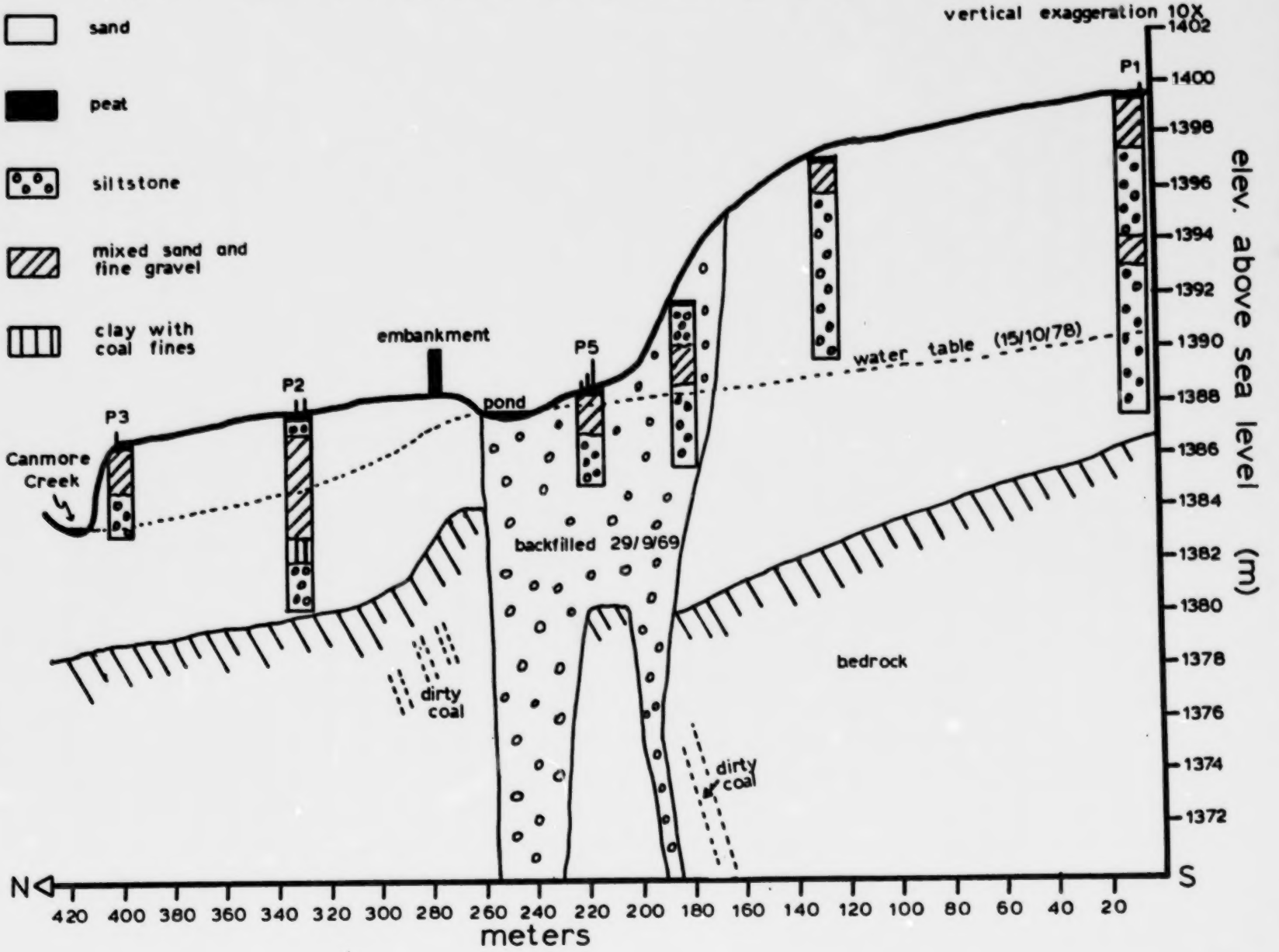


Table 9. Hydraulic head measure (in m)in Canmore piezometers (add 1300 m to each reading).

Instala-lation	Eleva-tion[1]	Depth[2] B.G.	Oct.10/78	Oct.15/78	Nov.20/78	Jan.16/79	Apr.25/79	July 12/79
P1	1339.850	12.05	90.0	89.985	89.96	89.95	89.96	90.195
P2A	1392.608	4.605	89.008	89.007	88.928	88.863	89.098	89.928
P2B	1392.886	7.635	89.021	89.011	88.941	88.866	89.106	89.926
P3	1391.551	4.165	88.146	88.145	88.156	88.151	88.226	88.446
P5A	1393.867	4.385	92.257	92.247	92.247	91.967	--	92.397
P5B	1393.126	2.990	92.191	92.246	92.256	91.976	--	92.406
P5C	1393.279	1.555	92.279	92.274	92.269	--	--	92.399
P6	1392.313	9.130	86.748	86.748	86.858	86.843	86.908	86.993

[1] Elevation above mean sea level in metres.

[2] Depth below ground in metres.

[3] Piezometer frozen.

small that measurement error is significant. Head measurements were taken with a homemade light tape and although the electronic components functioned very well, the actual measurement on the wire was made with a ruler from a fixed point, permitting small errors to occur. At Site 5, a downward movement of water occasionally occurred but the usual direction was upward. On the basis of these data, it appears that the water table is shallow and that discharge is occurring at the point of contact between the old highwall of the mine and the spoil material. The presence of many small springs in the area suggests that the bedrock is of low permeability (Davis and De Wiest 1966) and that water is probably draining through the spoil material from numerous fractures in the undisturbed bedrock.

A number of samples were taken for ^{18}O analysis both summer and winter of 1979. Oxygen-18 is a natural property of water which is sensitive to evaporation (Fritz et al. 1974; Fritz et al. 1975; Freeze and Cherry 1980; Wallis et al. 1979). Because lighter water molecules tend to evaporate first, the water which remains becomes progressively "heavier." For this reason snowmelt waters, rain waters, and surface waters usually have different ^{18}O contents and the influence of one upon the other can often be distinguished. Water samples were taken in small plastic bottles and sealed with wax to prevent any evaporation. The analyses were done at the Geochemistry Laboratory at the University of Waterloo on a VG Micromass 602D Twin mass spectrometer and the resulting data appear in Table 10. The accuracy of the analytical procedure is 0.2 parts per mille ($^{o}/oo$). All measurements were made with respect to Standard Mean Ocean Water which is arbitrarily assigned a value of 0 $^{o}/oo$. Snow in the Canmore area typically contains about -21.5 $^{o}/oo$, streams about -20 (reflecting snowmelt waters in groundwater discharge), and rain may be several parts per mille heavier because ^{18}O rich water molecules coalesce preferentially around dust particles in the atmosphere (Wallis et al. in press).

The data in Table 10 show that all of the ground and surface waters are heavily influenced by snowmelt. If large amounts of rain or surface waters (especially ponds) which have been exposed to evaporation had been present in the groundwater, the ^{18}O levels

Table 10. Oxygen-18 measurements from Canmore groundwaters.[1]

Installation	Date	/oo ^{0}
P2A	Jan. 16/79	-19.5
P2A	July 18/79	-20.2
P2B	Jan. 16/79	-20.1
P2B	July 18/79	-20.6
P3	Jan. 16/79	-19.8
P3	July 17/79	-20.5
P5A	July 18/79	-20.7
P5B	July 18/79	-20.6
P5C	Jan. 16/79	-19.9
P5C	July 18/79	-20.5
P6	Jan. 16/79	-20.8
Spring 1	July 18/79	-21.2
Spring 2	July 18/79	-21.2
Mine Effluent Spring	July 20/79	-20.7
Mine Effluent	July 16/79	-20.7
Canmore Creek	July 16/79	-19.3

[1] Accuracy of analysis: 0.2^{o}/oo

would have been significantly heavier. The uniformity throughout the samples over the year supports the hypothesis that snowmelt water is percolating through the rock and soil down the mountain slope and through the spoil material without becoming greatly contaminated by surface waters. This evidence, in conjunction with hydraulic head measurements, suggests that water does not percolate down from the ponds in the spoil material to any extent but is removed by surface drainage and evaporation. Groundwater of uniform consistency enters the spoil material from the south and percolates through it toward Canmore Creek. Some groundwater may be discharged onto the surface of the spoil where it either evaporates or drains away. The shallowest piezometers in Nests 2 and 5 show a very slight increase in ^{18}O from surface waters and Canmore Creek is significantly heavier because of its exposure to the atmosphere and its turbulence.

Measurements of hydraulic conductivity (K) and transmissivity (T) were made according to the bailing method of Cooper, Bredehoeft, and Papadopulos (1967) in July of 1979 and the data are reported in Table 11. Piezometer 1 is located in the trees above the disturbed zone and is considered to be a control piezometer. It is unfortunate that more control sites could not be established, but drilling time was limited and half a day was lost because of equipment failure. From the data in Table 11 it may be seen that the piezometers established in the spoil material (numbers P2A through P6) demonstrated a higher hydraulic conductivity than did the control piezometer, P1. The average hydraulic conductivity in the spoil material was 9.0×10^{-4} cm/sec and ranged from 1.3×10^{-3} to 8.4×10^{-5} cm/sec. Pliezometer 1 (6.7×10^{-7} cm/sec) is set into siltstone of the Kootenay Formation which has not been disturbed in any way so its lower permeability is not surprising. In the disturbed area, the same rock is more highly fractured and therefore higher in hydraulic conductivity. The water table above the mine may be expected to have a much higher gradient than in the spoil material because of the rapid elevation change. Piezometer 5B also shows a low permeability, perhaps providing a partial seal for the surface waters on top of the spoil material. This may have been caused by the packing action of heavy machinery maneuvering in a relatively small space.

Table 11. Hydraulic conductivity and transmissivity of Canmore piezometers after the method of Cooper et al. (1967).

Installation[1] Number	Hydraulic Conductivity (cm/sec)	Transmissivity (cm /sec)
P1	6.7×10^{-7}	4.1×10^{-5}
P2A	2.9×10^{-4}	1.7×10^{-2}
P2B	1.9×10^{-3}	1.1×10^{-1}
P3	1.4×10^{-4}	8.5×10^{-3}
P5A	1.3×10^{-3}	8.1×10^{-2}
P5B	8.4×10^{-5}	5.1×10^{-3}
P6	1.7×10^{-3}	1.0×10^{-1}

P5C could not be tested because of the extremely rapid recharge rate.

The small tributary to Canmore Creek which drains the spoil pile (designated 'Mine Effluent Creek') exhibits a similar seal, this time caused by several centimetres of clay. Water seeps out of the spoil over the clay and forms a small creek which finds its way through several pools to Canmore Creek. The bottom sediments are heavily stained with precipitated ferric hydroxide and aquatic macrophytes grow thickly. Iron oxidizing bacteria have been isolated from the slime matrix (Tim Ladd - pers. comm., telephone conversation, July 10, 1978.) The overall water quality does not appear to be seriously impaired, however, as a small population of Brook Trout (Salvelinus fontinalis) is well established in Mine Effluent Creek.

1.2.2.6 Groundwater Inorganic Chemistry. The Soils Branch Laboratory at Lethbridge kindly consented to analyze a set of samples from Canmore and the results are reported in Table 12. From these it may be seen that Mine Effluent Creek does not contain much copper, zinc, lead, cadmium, nickel, or chromium. Iron and manganese are also low in concentration, presumably because of chemical precipitation. The Mine Effluent Creek does, however, contribute to the calcium and magnesium load of Canmore Creek and the groundwater which was sampled from the spoil material also appears to be capable of adding divalent cations to Canmore Creek. Copper and zinc were found to be above the recommended drinking limits in the control piezometer, P1, although they are not in the spoil. Manganese is also higher than the recommended drinking limits in all the groundwater samples (Dept. of National Health and Welfare 1969). This does not appear to have any deleterious effects upon Canmore Creek. In P6, the sodium concentration is very much higher than in the other piezometers at the expense of calcium and magnesium. This is most unusual in the area and may have been caused by contamination from the bentonite balls used to seal the piezometer tips. In general, the groundwater in the spoil poses a problem with respect to manganese only.

Table 12. Metal analysis (in mg/L) from Canmore Creek, mine effluent, and piezometers.

Site	Fe	Ca	Zn	Mn	Ca	Mg	Na	K
Mine Effluent	.19	.02	.02	.05	126.2	42.5	9.2	1.2
Canmore Creek above Effluent	.05	.02	.01	.02	66.1	18.2	4.6	2.7
Canmore Creek below Effluent	.05	.02	.01	.02	96.2	20.6	4.6	1.2
P1	.05	.06	.08	.03	110.2	46.2	9.2	2.0
P2A	.13	.02	.01	.15	106.2	36.5	4.6	2.3
P2B	.14	.02	.05	.15	92.2	43.7	20.7	3.1
P3	.13	.02	.04	.63	104.2	48.6	23.0	4.3
P5A	.05	.03	.05	.40	118.2	42.5	6.9	2.3
P5B	.31	.02	.02	.06	110.2	40.1	6.9	2.3
P5C	.20	.02	.02	.65	112.2	37.7	4.6	2.0
P6	.15	.02	.03	.05	38.0	19.4	186.3*	5.9

Pb, Cd, Ni, and Cr are all below detection.

* Suspected bentonite contamination.

1.3 LITERATURE REVIEW

1.3.1 Organic Compounds Leached from Coal by Aqueous Solution

Although a considerable amount of work has been done on organic compounds which can be extracted from coal by organic solvents and various degradation procedures, very few workers have studied organic compounds leached from coal by water under natural conditions. It has been shown that a large number of organic chemicals may be extracted or prepared from coal despite its low solubility in neutral waters at low temperatures. Coal is composed to a large degree of humic and fulvic acids, reflecting its origin as the product of plant degradation. Approximate analysis of coal usually reveals a fixed carbon concentration of about 55% by weight for bituminous grades. Lignites are usually somewhat lower and anthracites may be higher. These percentages are variable and depend to a large extent upon the ash (mineral) content of the coal.

Humic substances may be divided into three categories with respect to their solubilities in acid or base. Humic and fulvic acids are both soluble in basic solutions but humic acid is precipitated in an acidic medium. Fulvic acid is soluble in both acid and base and humic is insoluble at any pH in water (Lawrence 1978, Manahan et al. 1978; Telang et al. 1976). Humic and fulvic acids are usually described as high molecular weight, polyelectrolytic macromolecules which are resistant to microbial degradation. The carbon skeletons are largely aromatic and oxygen-containing functional groups are prevalent. Carbohydrates and amino acids may be bound to the skeleton and released or taken up under different conditions. Metals, including calcium and magnesium, may form part of the skeleton of the molecule or may be present in ionic association as a salt (Manahan et al. 1979).

Campbell, Pellizzari, and Santor (1978) measured the concentration of some organic compounds in a coal seam near Gillette, Wyoming, prior to a gasification experiment. They found dissolved organic carbon to be present in amounts ranging from 3 to 8.5 mg/L, levels typical of groundwaters in general (Wallis et al. in press). A typical analysis quoted in their report contained 5.8 mg/L of dissolved carbon, of which 52% were hydrophilic compounds and 48%

were hydrophobic. In both cases, organic acids accounted for the majority of compounds. Further resolution was achieved through the use of a Gas Chromatograph-Mass Spectrometer for volatile organic compounds (Table 13). All of these compounds were present at very low levels, the highest being hexane at 32.4 μg/L. Toluene and methyl-pentane were the next most abundant compounds (11.3 and 8.7 μg/L, respectively), with several others present at very low concentrations. The concentration of phenolic compounds, a group which assumes major proportions after gasification, is very low, ranging from 0 to 2 μg/L. Numerous other compounds were also measured and found to be present in minimal concentrations, often less than 1 μg/L. Reference is made to Campbell, Pellizzari, and Santor (1978) for the complete list.

Although the preceeding reference was the only one found which analyzed organic compounds found in situ, some other measurements have been made of organic compounds in coal processing wastewaters and coal storage pile leachate. Unfortunately, all of these deal almost exclusively with inorganic constituents but some useful organic data may be gleaned. Ontario Hydro stockpiles coal from various sources to last through the winter and Featherby and Dodd (1977 in Davis et al. 1978) have made numerous chemical measurements. Among these were included five measurements of phenols whose average concentration in the leachates was quite low and ranged from μ0.001 to 0.012 mg/L. Wachter and Blackwood (1978) constructed an apparatus to simulate the leaching of coal by rainwater. They placed a mixture of coals from Alabama, Eastern Kentucky, Montana, Wyoming, Missouri, Illinois, and New Mexico under their apparatus and monitored the chemical quality of synthetic rainwater and the resultant leachate. They were primarily interested in organic compounds classed as hazardous by the Environmental Protection Agency but found that none of these exceeded 44 μ g/L in concentration (Table 14) and most were considerably less. In addition to these they did not observe any phenolic compounds at concentrations greater than 10μ g/L. A number of C19 hydrocarbons were also found, and the presence of C8 hydrocarbons, highly blanched adipates, di-n-butyl peroxide, and isobutylisobutyrate was suspected. All of these compounds were present at very low levels.

Table 13. Organic compounds found in groundwater by Campbell, Pellizzari, and Santor (1978).

Organic Compounds		Amount Present
Total Dissolved Organic Carbon		5.8 ± 3 mg/L
Hydrophilics:	Bases	4.0 ± 1% of DOC
	Acids	41.0 ± 7% of DOC
	Neutrals	7.0 ± 4% of DOC
Hydrophobics:	Bases	1 % of DOC
	Acids	36 ± 6% of DOC
	Neutrals	12 ± 5% of DOC
n-pentane		1.1 g/L
2-methyl pentane		8.7 g/L
3-methyl pentane		3.6 g/L
n-hexane		32.4 g/L
methyl cyclopentane		5.6 g/L
benzene		3.7 g/L
toluene		11.3 g/L
xylenes		0.6 g/L
p-ethyl toluene		1.2 g/L
n-decane		0.4 g/L
napthalene		4.7 g/L

Table 14. The concentration of toxic organic compounds in coal leachates found by Wachter and Blackwood (1978).

Compound	Concentration (µg/L)
2-chloronapthalene	14
acenaphthene	15
fluorene	14
fluoranthene	16
benzidine	14
benzo(ghi)perylene	44

In contrast to the simple leaching of coal storage piles by rainwater or the passage of groundwater through coal seams, the conversion of coal into synthetic fuels results in wastewaters significantly contaminated by organic compounds. Singer et al. (1978) have reviewed the results from several coal conversion plants around the world and presented a list of compounds identified. This list includes many chemicals within the broad classes: monohydric phenols dihydric phenols, polycyclic hydroxy compounds, monocyclic n-aromatics, polycyclic n-aromatics, aliphatic acids, and others. Most of these are present in concentrations ranging from 10 to 5600 mg/L, a large increase over the compounds found in the microgram per litre range found after simple aqueous leaching. These authors also carried out biotreatability experiments with many of these compounds, particularly the phenols, which comprised over 60% of the chemicals found in coal conversion wastewaters (Table 15). Many of these are biodegradable to a degree but a considerable amount of work remains to be done to discover the optimum conditions for carrying this out. Although not discussed by Singer et al., humic substances are also present in coal conversion wastewaters. Manahan et al. (1978) have considered these in the light of their use in pollution control because of the ability to act as acids and bases and their properties of chelation, precipitation with hydrogen or metal ions, sorption or organic compounds, foaming, and flocculation. They were able to show that coal humic substances were able to enhance the removal of organic compounds such as benz(a)pyrene, phenol, and benzoic acid.

The literature available which deals with natural organic compounds leachable by water from coal was found to be sparse. It is evident, however, that a small background assemblage of organic compounds derived from coal may be expected to be present in any water which leached through it. The toxic compounds which have been found are too low in concentration to cause problems. The humic substances which make up coal are known to be complex and to react with both other organic chemicals and metals.

Table 15. Summary of environmental behavior of classes of organic coal conversion effluent constituents.[1]

	Acute Toxicity	Chronic Effects	Wastewater Removal Efficiency	Microbial Degradation	Bioaccumulation Potential	Information Avalialbe
Phenols	High	Low	High	Rapid	Low	Much
Monoaromatics	Moderate	Low	Moderate	Moderate	Low	Moderate
Polycyclic Aromatics	High	High	Low	Slow	High	Moderate
Aromatic Amines	Moderate	High[2]	Low	Slow	Moderate[2]	Little
Thiophenes	Moderate	High[2]	Low[2]	Slow[2]	Moderate[2]	Little

1 After Singer et al. (1978)

2 Insufficient information to support valid conclusions.

2. ORGANIC GEOCHEMISTRY

2.1 METHODOLOGY

2.1.1 Field Sampling

Groundwater samples were taken from wells and piezometers by means of a bailer constructed from PVC pipe equipped with a foot valve. Sampling trips at monthly intervals were made from September of 1978 to December of 1979. Because of the length of time required for analysis and the other laboratory operations which were part of this study, it was not possible to sample more than one mine site per month. Consequently, each mine was visited at approximately 2-month intervals.

2.1.1.1 Preliminary Geochemistry. At the beginning of this project, a number of experiments were carried out to determine the best sampling procedure. In order to evaluate the stability of the organic compounds to be measured, it was necessary to know the temperature, Eh, pH, and oxygen content of the groundwaters to be sampled. To measure these, a flow cell was constructed of plexiglass consisting of a square box open at the top and an open cylinder, 9 cm in diameter and 8 cm in height, glued to the centre of the floor of the container. The top of the cylinder was covered with a thin plexiglass sheet which had been perforated to admit the probes of an Eh/pH meter, an oxygen probe, and a thermometer. Inlet tubes were provided so that groundwater could be pumped by the probes without coming into contact with the atmosphere, run out through the base of the cylinder, rise up in the box, and overflow. The large volume of water surrounding the cylinder in the box maintained thermal stability. Water was pumped into the box using a Masterflex 6 mm peristaltic pump made by the Horizon Ecology Company. Eh and pH were measured with a Sargent-Welch Model PBX meter and oxygen with a Yellow Springs Instrument Company Model 54RC oxygen meter. All instruments were battery operated and field portable. The difficulty imposed by this apparatus was that water could not be pumped up for more than 8 m because of the limitations

of suction pumps. In order to reach deeper wells, a Rapidayton Model 5TA pump with a 5 cm injector was tried but the pumping action was so violent that temperature and gas content were disturbed. Another attempt using an air lift pump obtained from Dr. E. Wallick of the Alberta Research Council also failed for the same reason. Attempts to force water from deeper wells up a 6 mm tube by introducing positive pressure at the top could not deliver enough water for analysis because too much water was forced out the bottom of the piezometers. At this point, the use of the probe box to measure these parameters in deep wells and piezometers was abandoned. In practice this meant that the piezometers at Canmore could be sampled except for P1, but only P2C could be reached at Wabamun. Piezometer 1 was sampled using a bailer so that measurements could be made, but this meant that the water had been exposed to the atmosphere. Temperature and pH had already been measured by the Groundwater Branch personnel on a number of occasions at Wabamun and these data were available. The decision made at that time was to determine the optimum sampling procedure on the basis of existing data from the measurements made at Canmore and from the data collected by Groundwater Branch. The geochemical data from Canmore, upon which this procedure was based, are reported in Figure 4 and the data from Wabamun may be found in the Whitewood report (Anon. 1979).

These parameters were measured at Canmore on September 26, 1978 and checked again the following summer (July 20, 1979). In the fall of 1978, pH ranged from 6.9 to 7.6 through Installation Numbers 1 to 8 which correspond to a transect through Reclamation Site 2 from the control piezometer upstream (P 1) to the test peizometers placed in the spoil bank (P7 and P8) by the stream. These data show that pH was slightly higher on that occasion in the control piezometer than in the mine piezometer. The same trend was observed in the summer of 1979 when the pH ranged from 6.7 to 7.9. Higher pH's have been recorded but they were believed to have been caused by cement contamination (Anon. 1979). The average pH measured in the field was about 7.6 at Wabamun, as it was at Canmore and no large change was observed between installations.

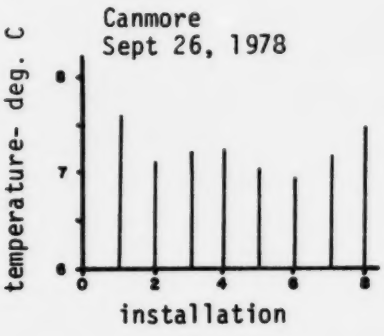
The temperature of the groundwater was more uniform in the fall of 1978 and averaged 9°C. Summer temperatures were slightly higher in the shallow piezometers but the average did not change greatly. Temperatures measured at Wabamun all fell within the same range. Oxygen was measured at all installations at Canmore with piezometers 2, 4, 6, and 8 showing no oxygen at all. A concentration of 5 mg/L was observed in the control piezometer (P1) in September 1978, but this may have been an artifact introduced from the bailer sample. Because P1 recharged much more slowly than the other piezometers, the water had been in the standpipe for several hours before oxygen was measured. The oxygen content in P1 was only 2.1 mg/L in the summer of 1979, using the same sampling method. At this time a spring (Installation Number 14) was sampled using the probe box in an effort to determine the oxygen content of groundwaters before they passed through the minesite. The oxygen content was found to be 9.3 mg/L, but a similar spring coming from the base of the spoil pile was almost as high (7.3 mg/L). It appears, therefore, that oxygen concentrations are lower in the groundwater which has passed through the minesite, but the concentration measured in the control piezometer may be overestimated. For the purpose of establishing a sampling procedure, it was concluded that the amount of oxygen present is variable both between installations and within the same piezometer at different times of the year (see Figure 4).

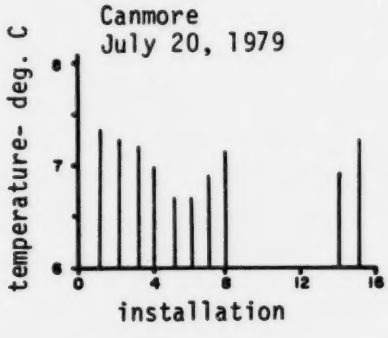
The measurement of Eh with a probe has been criticized in the literature (Stumm and Morgan 1970) because complex natural systems are not always in equilibrium and the readings obtained may not represent reversible Nernst potentials. Eh may also be calculated using the relative proportions of dissolved species such as Fe^{2+}, Mn^{2+}, HS^{-}-SO_4^{2-}, or CH_4-CO_2 (Stumm and Morgan 1970). In this case, the oxidation of Fe^{+} by water according to the reaction below was used:

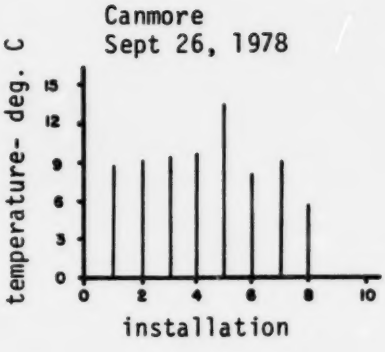
$$Fe^{2+} + 3H_2O \qquad Fe(OH)_3 + 3H^{+} + 3e^{-} \qquad \text{...Equation 1}$$

and it was assumed that the system was in equilibrium. Eh may be calculated from this reaction by using the measured concentration

Figure 4. Geochemical data collected at Canmore.







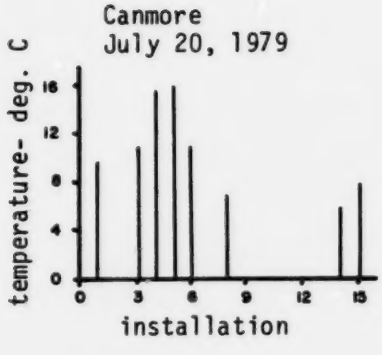
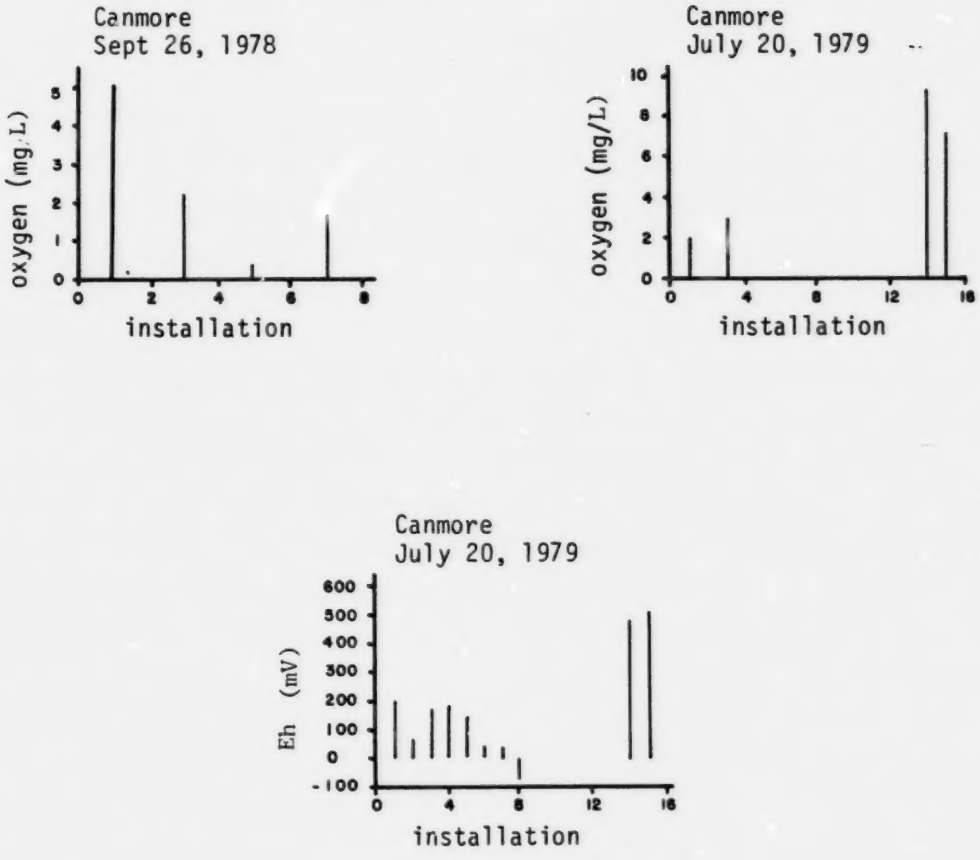


Figure 4. Concluded.



of Fe^{2+} and pH in the substituted Nernst equation below (Garrels and Christ 1965):

$$Eh = E^0 + 0.059 \log [H^+]^3 [Fe(OH)_3]/[Fe^{2+}]$$

...Equation 2

where E^0 = +1.06 Volts (Krauskopf 1967) and $Fe(OH)_3$ = 1 by convention because it is insoluble in water. This method was used to measure Eh in 11 wells and piezometers at Wabamun. The concentration of Fe^{2+} was measured using the phenanthroline method (APHA 1975) in the field by means of a portable spectrophotometer made by the Hach Company. The results are quoted in Table 16 but the analytical difficulties encountered render these data suspect. Although the probe and the iron measurement method were compared in the laboratory and were found to agree within 0.005 V, the clay content of the groundwater interfered with the determination of iron in the field. The turbidity of the solution required that the red phenanthroline-iron complex be extracted with potassium perchlorate and nitrobenzene before the absorbance could be read. Unfortunately, a considerable portion of the Fe^{2+} appeared to be bound to the clay and was lost during the extraction.

These data and those collected at Canmore indicate that Eh is generally slightly positive and that small amounts of oxygen are usually present. Garrels and Christ (1965) state (p. 137) that natural waters which contain oxygen may be expected to have an Eh which can be calculated approximately according to the equation below:

$$Eh = 0.70 - 0.06\ pH$$

...Equation 3

The average pH from Table 16 is 7.5 so the expected Eh would be 0.250 V. This is more positive than the experimentally observed values, but the oxygen content is not as high in these groundwaters as in waters in equilibrium with the atmosphere. Although these

Table 16. Geochemical data collected at Canmore.

Installation	Fe^{2+} (mg/L)	pH	Temperature (^{o}C)	Eh (Volts)
WC2	3.5	7.4	8.0	-.002
PC2A	5.5	7.8	7.0	-.084
PC2B	6.4	7.4	6.5	-.017
PC2C	1.4	7.2	7.0	+.058
PC2D	8.4	7.6	7.0	-.060
PC2E	1.2	8.0	9.0	-.079
A22	1.0	6.4	8.0	+.208
W4	31.0	7.5	10.0	-.039
P4A	5.5	7.0	9.0	+.052
P4B	22.6	6.5	9.0	+.163
P4C	22.6	6.6	8.5	+.139
Measurements Using Probe Box				
P2C	--	6.5	8.1	---

measurements of Eh are subject to error, they fall close to the expected range and do not indicate strongly reducing conditions.

The results of the preliminary geochemical work indicate that groundwaters are generally mildly oxidizing, have an average temperature between 4 and 10°C, and contain only modest amounts of oxygen. The range in temperatures suggested that samples should be chilled in an ice chest but not frozen. This was accomplished by packing them tightly in specially made wooden boxes with a thin layer of insulation. The containers were tightly stoppered to prevent any further influx of oxygen or degassing of carbon dixoide or hydrogen sulphide. The choice of container type and the permissible time of storage were decided upon on the basis of the experiments described below.

2.1.1.2 Storage Experiments. In the absence of data in the literature pertaining to the best method of storage of samples for organic analysis, it was decided to undertake a series of experiments to evaluate preservation methods. The effects of storage in glass (Wheaton BOD bottles) or polyethylene (Nalgene) bottles over time were evaluated by filling a number of bottles with filtered water and sacrificing bottles at intervals for dissolved organic carbon analysis using the potassium dichromate method of Maciolek (1962). It was also considered necessary to test the effects of freezing, chilling, acidifying, and poisoning with mercuric chloride on the concentration of dissolved organic matter with time. Accordingly, a simple matrix of samples was prepared according to the following scheme. One set of samples was left on the bench to serve as a control.

	Mercuric Chloride	Acid pH 3	Room Temp.	5°C	Frozen
Glass Bottles	+	+	+	+	-
Plastic "	+	+	+	+	+

Samples were not frozen in glass bottles because of breakage. Water was sampled from Barrier Creek behind the Kananaskis Centre, filtered in a batch through an acid washed Whatman GF/C glass fiber

filter, and divided into glass and plastic sample bottles according to the matrix above. Five replicates were made of each of the nine combinations listed for periodic sacrifice and the results are reported in Figure 5. Surprisingly, very little variation was observed. In all cases the dissolved organic matter in the containers remained in solution for about 2 weeks and then dropped to approximately 30% of the original concentration. This trend appeared to be completely independent of all sample treatments. In order to confirm these findings, the experiment was repeated with a fresh water sample and the results are reported in Figure 6. The same trend was found; the concentration of dissolved organic matter declined (after only 1 week this time) and the different treatments seemed to have no effect.

The question was asked: where is the organic matter going? It seemed improbable that microbial degradation was responsible considering the harshness of some of the treatments, so it was suggested that the organic material was precipitating on the walls of the flask. In order to test this hypothesis, a third experiment was set up. This time the water sample was filtered in the same manner and divided into 28 Erlenmeyer flasks which had all been washed in fresh acid baths. Two flasks were sacrificed at a time and the contents poured into a fresh Erlenmeyer flask. Organic carbon analyses were performed on all four flasks in order to determine whether the organic carbon was still on the walls of the original flask or in the water sample. The results from this experiment are not clear (Figure 7); although the organic matter dissolved in the water sample decreased slowly with time, so did the total organic matter in the flask. The concentration of dissolved organic matter in the original water sample was very low (0.8 mg/L) and it was difficult to detect small changes at these levels. In order to overcome this problem, some well water from Wabamun (Well 4) was obtained which contained about 6.5 mg/L organic carbon. The experiment was repeated with this water and the results appear in Figure 8. This time, a fairly even deposition of about 0.5 mg/L was observed to the flask walls and the total amount of organic carbon remained constant.

Figure 5. First storage experiment.

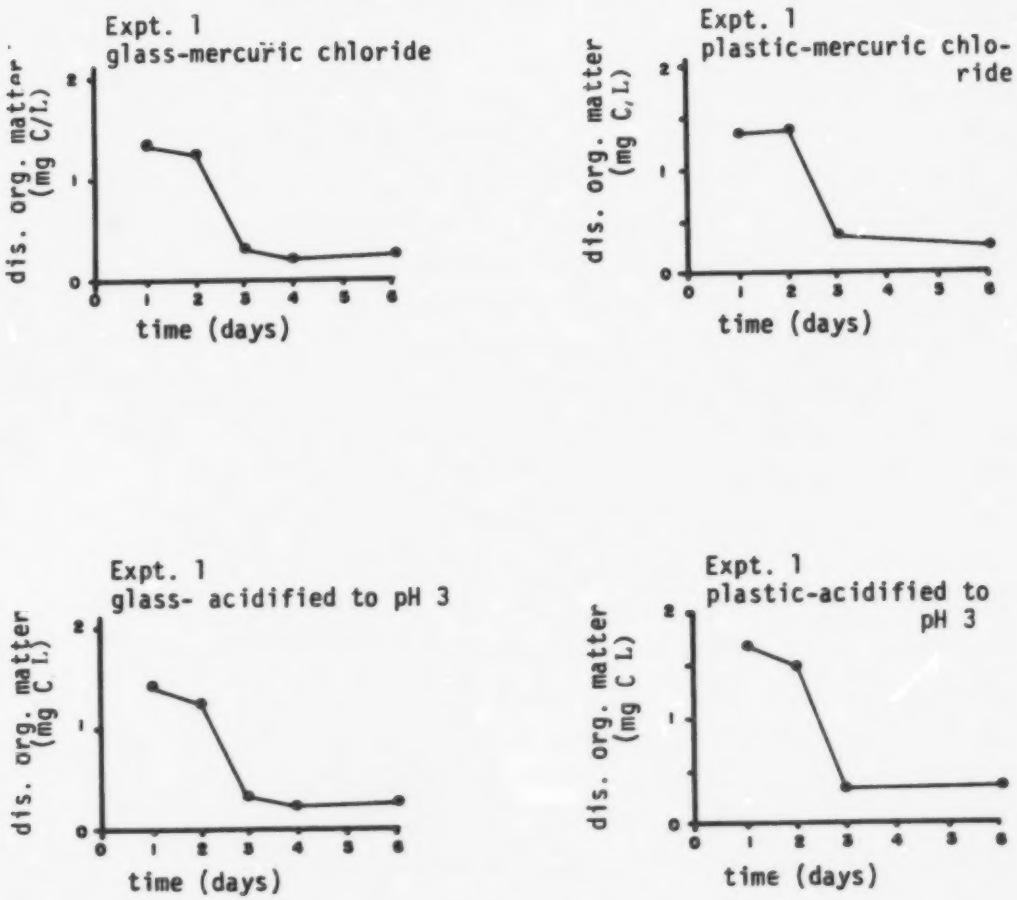
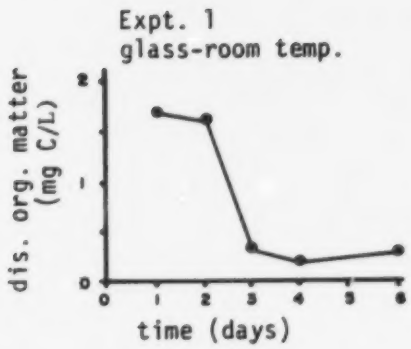
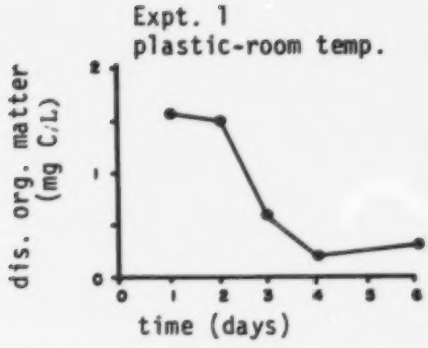
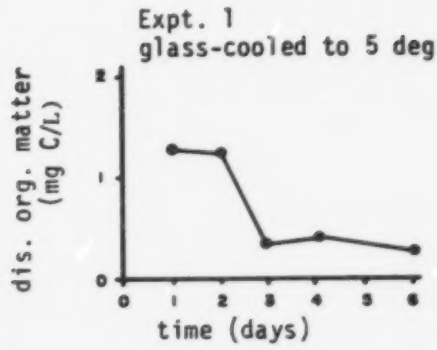
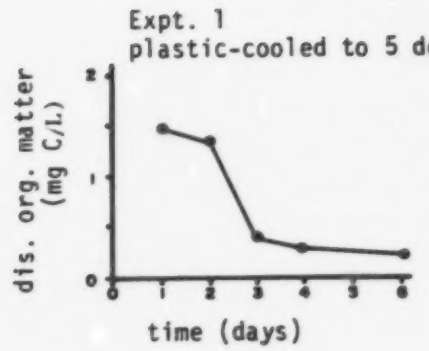


Figure 5. Concluded.









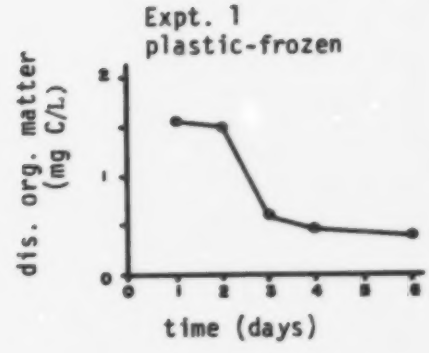


Figure 6. Second storage experiment.

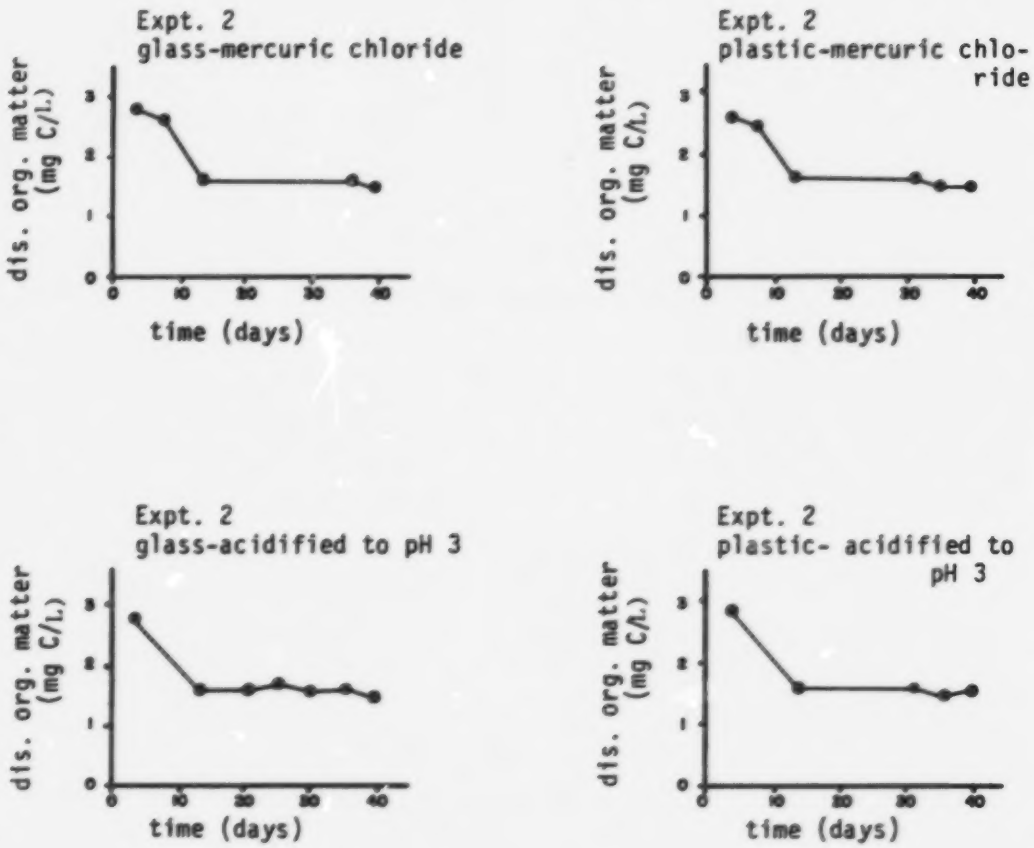


Figure 6. Concluded.

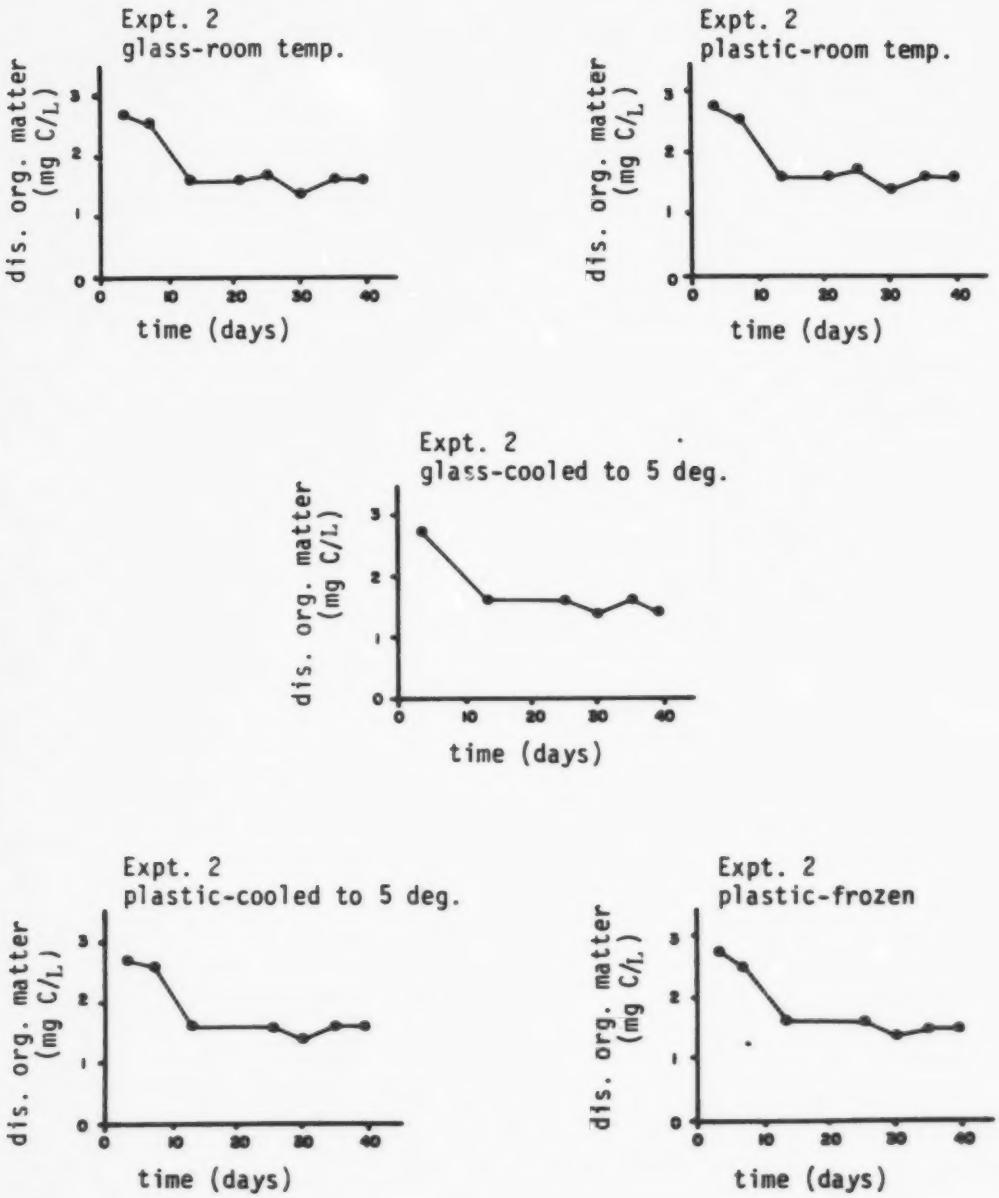


Figure 7. Third storage experiment.

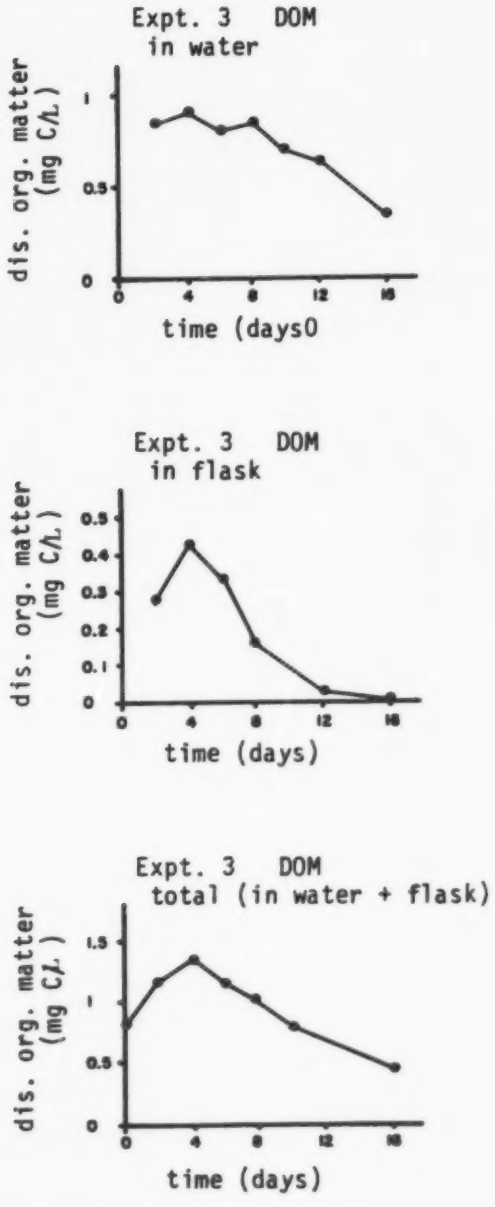
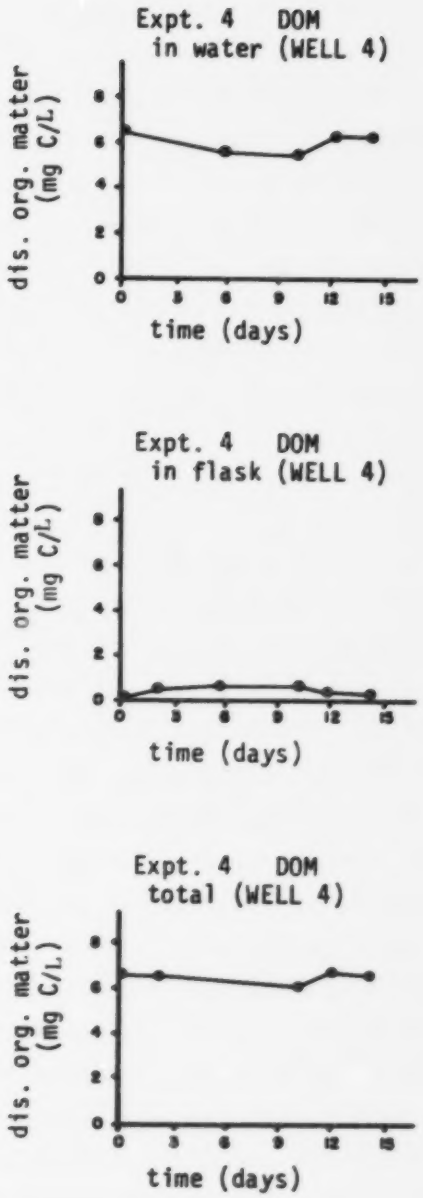


Figure 8. Fourth storage experiment.



The conclusion made from these storage experiments was that the mode of storage was much less important than the length of storage time. Samples which are more than 1 week old are suspect because of deposition of organic matter on the flask walls and perhaps other unquantified mechanisms. Plastic bottles were used because of their convenience in the field and all analyses were commenced as soon as they were returned to the laboratory, usually within a few hours of sampling. It may be argued that small amounts of plasticizers may be leached from Nalgene bottles but these effects were undetectable by the analytical methods used in this study. If more detailed analysis is contemplated using sensitive equipment, glass is preferable (M. Strosher - pers. comm., telephone conversation Sept. 12, 1978). Nalgene bottles also offer the advantage of efficient sealing, an important consideration when dealing with water samples which are not in equilibrium with the atmosphere. Plastic is not entirely impervious to oxygen, but diffusion rates are slow and glass is easily broken. The best solution is to seal bottles well, analyze as quickly as possible, and maintain field temperatures during transit.

2.1.2 Choice of Organic Analyses

The range of organic compounds which may be found in ground and surface waters is enormous, too large to ever be fully described for one water sample. Fortunately, there is rarely any reason to undertake an ultimate analysis of this sort and analyses of water samples made on a routine basis usually include a measure of total organic carbon only. Occasionally, the sample is filtered through an ashed glass fiber filter and the filtrate analyzed for organic matter. This fraction is known as dissolved organic matter (DOM). The present study required that organic matter be analyzed in much greater detail than this but, at the same time, a large number of samples were necessary to adequately describe both minesites. Because some of the tests take an appreciable length of time, the number of different analyses had to be kept to a minimum. The organic chemical parameters selected had to be quantitatively important in order to fulfill the objective of describing the organic matter present, but it was also considered necessary to measure the concentrations of organic compounds which are of

nutritive value to the bacteria because the activities of these organisms can influence inorganic chemistry.

It is well known that organic matter in natural waters consists mainly of large molecular weight compounds which are relatively impervious to microbial attack (Wallis et al. in press; Larson 1978; Lawrence 1978). These are the humic and fulvic acids which are formed in soil and water from the breakdown of plant and animal material. They are also present in coal (Campbell, Pellizzari, and Santor 1978) and, for these reasons, it was considered essential to measure the concentration of these compounds. Groundwater may be expected to contain significant quantities of tannins and lignins from plant material (Hackett et al. 1977; Wallis et al. 1979) in soil so an analysis of these compounds was also considered essential. In considering the nutrition of bacteria, carbohydrates and amino acids (both free and combined as proteins) are important so these were also included. The analysis of carbohydrate is relatively easy but amino acids are much more difficult so only the former was done on a routine basis. These analyses, in conjunction with a measurement of dissolved organic carbon, were chosen for this study. A few measurements of simple phenols were also undertaken.

2.1.3 Organic Analytical Methodology

Because almost all fresh well and piezometer samples contained appreciable amounts of clay in suspension, samples were filtered through acid washed, combusted (at 550°C) Whatman GF/C glass fiber filters. If this had not been done, the colourimetrically based analyses could not have been carried out because of turbidity. The concentration of dissolved organic matter in most samples was less than 6 mg/L, most of which were humic and fulvic acids. The levels of carbohydrates, tannins and lignins, and amino acids were correspondingly low, rendering accurate analysis difficult. For this reason, they were all concentrated ten-fold in a Cyclone-type flash evaporator (Quickfit Corp.). This necessitated heating the samples at 38°C under vacuum which should not have caused any profound chemical changes (proteins are probably the most fragile organic compound present which were measured and even they

do not denature below 50°C - Lehninger 1970). Measurements of total organic carbon in the distilled water confirmed that it all remained in the sample concentrate. Another problem which may be caused by this method is the co-precipitation of organic matter with inorganic salts (Otsuki and Wetzel 1973). For this reason precipitated salts were mixed as well as possible and carefully included in all chemical tests. The nature of these analyses was such that the salts became re-dissolved in their eventual reaction mixtures. The error associated with all analyses was less than 10% as determined by repetitive tests.

2.1.3.1 Tannins and Lignins. Water samples were analyzed for tannins and lignins colourimetrically by the phosphomolybdic acid method (APHA 1976). Tannic acid was used for the standard and no interferences were found.

2.1.3.2 Carbohydrates. Dissolved carbohydrates were determined by the phenol-sulphuric acid method of Dubois et al. (1956) using glucose as a standard. After filtration and concentration, 2 mL of sample were pipetted into a 125 mL Erlenmeyer flask and 2 mL of phenol reagent were added. Sulphuric acid (10 mL) was added while the sample was being mixed by shaking. The flask was covered with aluminum foil and allowed to stand for 1 hour before the absorption was measured at 490 nm in a 1 cm cell. Some problems occurred with interferences by nitrates. These were obviated by trapping the carbohydrates on an XAD ion exchange resin and allowing the inorganic constituents to pass on through the column. The organic material was recovered by eluting with 0.01 N NaOH.

2.1.3.3 Phenols. A photometric method (APHA 1975) based on the reaction of steam distillable phenolic compounds with 4-aminoantipyrene at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide, was used. The antipyrene colour formed by this reaction was measured in a chloroform solution at 460 nm. This method is satisfactory for simple phenols but cannot detect complex polymeric phenol groups. The analysis of these compounds would have required extensive gas chromatographic work which was not feasible within the time frame of this study.

2.1.3.4 Dissolved Organic Carbon. Samples were analyzed for dissolved organic carbon using a slight modification of the wet oxidation method of Maciolek (1962). Ten mLs of concentrated sample were pipetted into a 125 mL Erlenmeyer flask which had been cleaned in a chromic acid bath. The contents of the flask were evaporated to dryness at 90°C following which 10 mLs of H_2SO_4 (concentrated S.G. 1.82) and 5 mLs of 0.05 N $K_2Cr_2O_7$ were added and the contents of the flask swirled. The oxidation of the organic matter present caused the colour of the dichromate solution to turn from orange to green, depending on the amount present. Colour development was allowed to proceed for three hours at 90°C. Distilled water (50 mls) was then added to each flask and the absorbance read at 340 nm. This method was very sensitive but the linear working range was only from 0 to 8 mg C/1. Potassium biphthalate was used for a standard.

2.1.3.5 Humic and Fulvic Acids. These were determined after the method of Telang et al. (1976) in the form of dissolved organic carbon. The basicity of the sample was adjusted to pH 0.9 using 0.1 N NaOH in order to bring both humic and fulvic acids into solution. The filtrate was then divided into two parts. One part was adjusted to pH 7.0 with HCl and the organic carbon content was determined. The other part was acidified to pH 2 with HCl and refrigerated for 5 d in a N_2 atmosphere. The acidic solution was then filtered to remove precipitated humic acid and the organic carbon content of the filter and of the solution were determined. The average of these two figures was considered to be the humic acid content. Fulvic acid could only be determined as the difference between the total organic carbon content of the original sample and the sum of the other measured organic constituents. For this reason, all of the "fulvic acid" data in this report were calculated by difference and contain small amounts of other organic constituents such as amino acids. A better method would have been the solvent extraction method of Strosher and Peake (1976), but the amount of work involved made this impractical for a large number of samples. Lawrence (in prep.) presents an alternate photometric method for the determination of tannins, lignosulphonic acid, and

fulvic acid. An attempt to use this method failed because of the presence of other highly coloured clay minerals in the samples. Efforts to trap the organic matter on XAD resin resulted in incomplete recovery so this method was abandoned.

2.1.3.6 Amino Acids. Free and combined amino acids were determined separately. Procedures for sample concentration, hydrolysis and deionization were similar to those of Degens and Reuter (1966). The amino acid analysis was carried out by gas chromatography using the techniques of Roach and Gehrke (1969).

The separation of free amino acids from combined amino acids was done with ion exchange columns. A slurry of Baker CGC 240 ion exchange resin in concentrated NH_4OH was poured into a 25 mL burette (plugged with glass wool) until an 8 mL bed of resin was formed. The bed of resin was washed three times with the following sequence of solutions: 2 volumes concentrated NH_4OH, 2 volumes distilled water, 2 volumes 6N HCl and finally 2 volumes distilled water.

One litre of each water sample was filtered through a 0.45 μ glass fiber filter and concentrated at 50^{o}C under vacuum in a rotary evaporator to 5 mL. The pH of the concentrate was adjusted to 4 by dropwise addition of 4 N HCl and placed on a column of Baker CGC 240 ion exchange resin. The column was eluted with 32 mL of distilled water which removed the neutral organic matter plus dissolved combined acids. The column was then eluted with 64 mL 2N NH_4OH to remove the free amino acids.

For derivatization, the eluate containing the free amino acids was reduced to dryness in a rotary evaporator under vacuum at 50^{o}C. Five hundred L of 0.1 N HCl were added and the contents swirled around to dissolve the amino acids. Two hundred and fifty μL of this solution were transferred to a small vial and reduced to dryness under N_2 with gentle heating. One hundred L of 3M butanol in HCl (prepared by bubbling HCl gas into butanol until 2.73 g was dissolved in 25 mL or 20.89 g butanol) were added, the vial was tightly sealed with a teflon lined solid cap and heated at 100^{o}C for 15 minutes; the sample was cooled and reduced to dryness

by evaporation under a stream of N_2.* Twenty μL of methylene chloride were added to the residue and 2 to 10 μL of solution were injected into the gas chromatograph.

The 32 mL of eluate from the ion exchange column containing the dissolved combined acids were reduced to dryness. Six mL of 6N HCl were added to dissolve the solids, and the eluate was transferred to a 15 mL culture tube. The tube was tightly sealed with a teflon lined cap and heated for 16 hours at 100°C to hydrolyze the combined acids. After cooling, the tube was centrifuged for 10 minutes to remove any suspended precipitate. The acid solution was transferred to a 50 mL conical flask and reduced to dryness. Five mL of water were added and the pH of the solution was adjusted to 4. The solution was placed on a previously prepared column of ion exchange resin, washed with 32 mL of water and the free amino acids eluted with 64 mL of 2N NH_4OH. These amino acids were transferred into a 0.1 N HCl solution and the N-trifluoroacetyl n-butyl esters formed as described for the free amino acids.

A Hewlett Packard Model 5750 gas chromatograph was used to analyze the derivatized amino acids. It was fitted with a 1928 mm by 2 mm coil shaped glass column packed with Regis Chemical Company TABSORB precoated column packing. The helium carrier gas flow rate was 50 mL/min; combustion gases were air and hydrogen with flow rates of 450 and 50 mL/min, respectively. The column oven temperature was programmed at 4°C per minute from 50 to 220°C, with a post injection interval of 5 minutes, and then held isothermally at the upper limit for 15 minutes. The entire procedure was tested using standard mixtures containing 2.5×10^{-7} g/ L each of 16 amino acids.

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* One hundred μL of methylene chloride and 25 μL of trifluoracetic anhydride were added and the mixture was heated in a tightly closed vial for 10 minutes at 138°C. The sample was cooled and the solvent removed under N_2.

2.2 RESULTS OF FIELD SAMPLING

2.2.1 Canmore - General Results

The data collected over a 12-month period were analyzed with respect to the relationships between parameters, the depth of the installation sampled, and changes occurring over a cross-section through Reclamation Site 2. Linear regressions were calculated between all possible combinations of parameters using all of the data. The results are reported in Tables 17 and 18, but few significant relationships are evident. Tannins and lignins could not be correlated significantly with any other variable and neither could carbohydrates. Humic acid was weakly related to fulvic acid ($r = 0.48$) and more strongly related to dissolved organic matter ($r = 0.65$). Fulvic acid was strongly related to dissolved organic matter although this may have been caused by the analytical limitations discussed in Section 2.1.3.5. The preponderance of refractory fulvic acids in natural waters (Lawrence 1978; Larson 1978; Wallis et al. in press) has been well documented in the literature. As coal contains large amounts of these high molecular weight materials, this relationship is understandable. All organic data were converted to the equivalent weight of carbon in order to facilitate comparisons and the calculations of fulvic acids by difference.

2.2.1.1 Tannins and Lignins. Tannins and lignins were generally low at Canmore, less than 1 mg/L expressed as the equivalent weight of carbon. The average values found for each sampling site are reported in Table 19. Although the standard deviations are as large as the means, the range was only 0.03 to 0.1 mg/L for all installations. Tannins and lignins in the control piezometer (P3) and in the creek which drains the spoil bank (Mine Effluent Creek) are shown in Figures 9, 10, and 11. These figures show the concentrations of all of the organic parameters measured graphed against time expressed as the number of days since January 1, 1978. The time span covered by these graphs is from October 1978 to September 1979. From these, it appears that concentrations of tannins and lignins are not very much different, but higher levels are higher

Table 17. Tests of relationships between all combinations of parameters measured at Canmore using linear regression analysis.

X-Parameter	Y-Parameter	r	r^2
Tannins + Lignins	Carbohydrates	0.10	0.01
"	Humic Acid	0.21	0.04
"	Fulvic Acid	0.03	0.0009
"	Dissolved Organic Matter	0.07	0.005
Carbohydrates	Humic Acid	0.13	0.02
"	Fulvic Acid	0.37	0.14
"	Dissolved Organic Matter	0.13	0.02
Humic Acid	Fulvic Acid	0.48	0.23
"	Dissolved Organic Matter	0.65	0.42
Fulvic Acid	Dissolved Organic Matter	0.97	0.94
Bacteria (Direct Count)	Tannins + Lignins	0.27	0.07
"	Carbohydrates	0.009	0.00008
"	Humic Acid	0.03	0.0009
"	Fulvic Acid	0.12	0.01
"	Dissolved Organic Matter	0.26	0.07
Bacteria (Plate Count)	Tannins + Lignins	0.29	0.08
"	Carbohydrates	0.36	0.13
"	Humic Acid	0.10	0.01
"	Fulvic Acid	0.77	0.59
"	Dissolved Organic Matter	0.69	0.48

Table 18. Tests of relationships between various parameters and depth at Canmore using linear regression analysis.

Parameter	r	r^2
Tannins + Lignins	0.13	0.017
Carbohydrates	0.11	0.01
Humic Acid	0.06	0.004
Fulvic Acid	0.09	0.008
Dissolved Organic Matter	0.14	0.02
Phenols	0.35	0.12
Bacteria (Direct Count)	0.11	0.01
Bacteria (Plate Count)	0.10	0.01

Table 19. Average values found at Canmore for all organic parameters measured. The results are reported in milligrams of carbon per litre.

Sampling Site	Tannins + Lignins		Carbohydrates		Humic Acid		Fulvic Acid		Dissolved Organic Matter	
	Mean	___	Mean	___	Mean	___	Mean	___	Mean	___
1	.03	.03	.09	0.1	.38	.3	1.6	.9	1.9	1.1
2A	.1	.09	.08	.08	.34	.26	1.2	.8	1.6	.7
2B	.05	.03	.1	.09	.21	.17	1.2	.9	1.04	.9
3	.1	.1	.07	.07	.26	.19	1.41	.77	1.49	.75
5A	.09	.04	.33	.42	.31	.98	.38	.36	1.34	.79
5B	.09	.08	.08	.10	.34	.31	.83	.44	1.15	.31
5C	.05	.03	.05	.08	.43	.31	.99	.68	1.43	.72
6	.06	.02	.08	.12	.31	.17	1.46	.63	1.36	.27
Canmore Crk Above Effluent	.03	.02	.05.	.06	.25	.20	1.38	.63	.25	.20
Canmore Crk Below Effluent	.03	.02	.06	.08	.34	.21	1.23	.91	1.56	.94
Mine Effluent	.04	.02	.04	.07	.38	.08	1.29	1.25	1.60	1.08
Maximum	.1		.33		.43		1.6		1.9	
Minimum	.03		.04		.25		.83		.25	
Mean	.06		.09		.32		1.23		1.34	

Figure 9. Concentrations of organic parameters measured over time at Canmore in Piezometer 1 (Control) expressed in milligrams of carbon per litre.

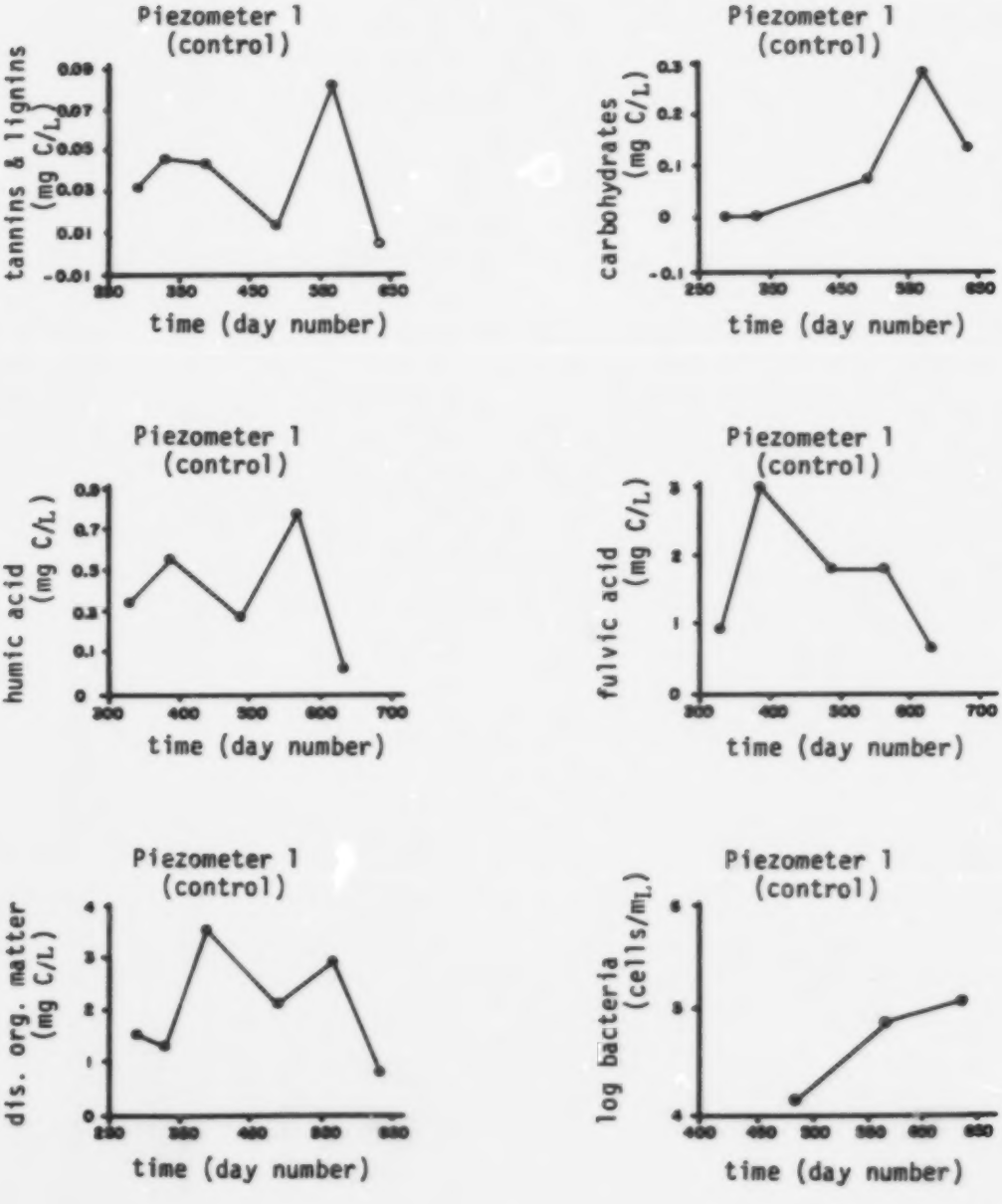


Figure 10. Concentrations of organic parameters measured over time at Canmore in Piezometer 3 (Mine Spoil) expressed in milligrams of carbon per litre.

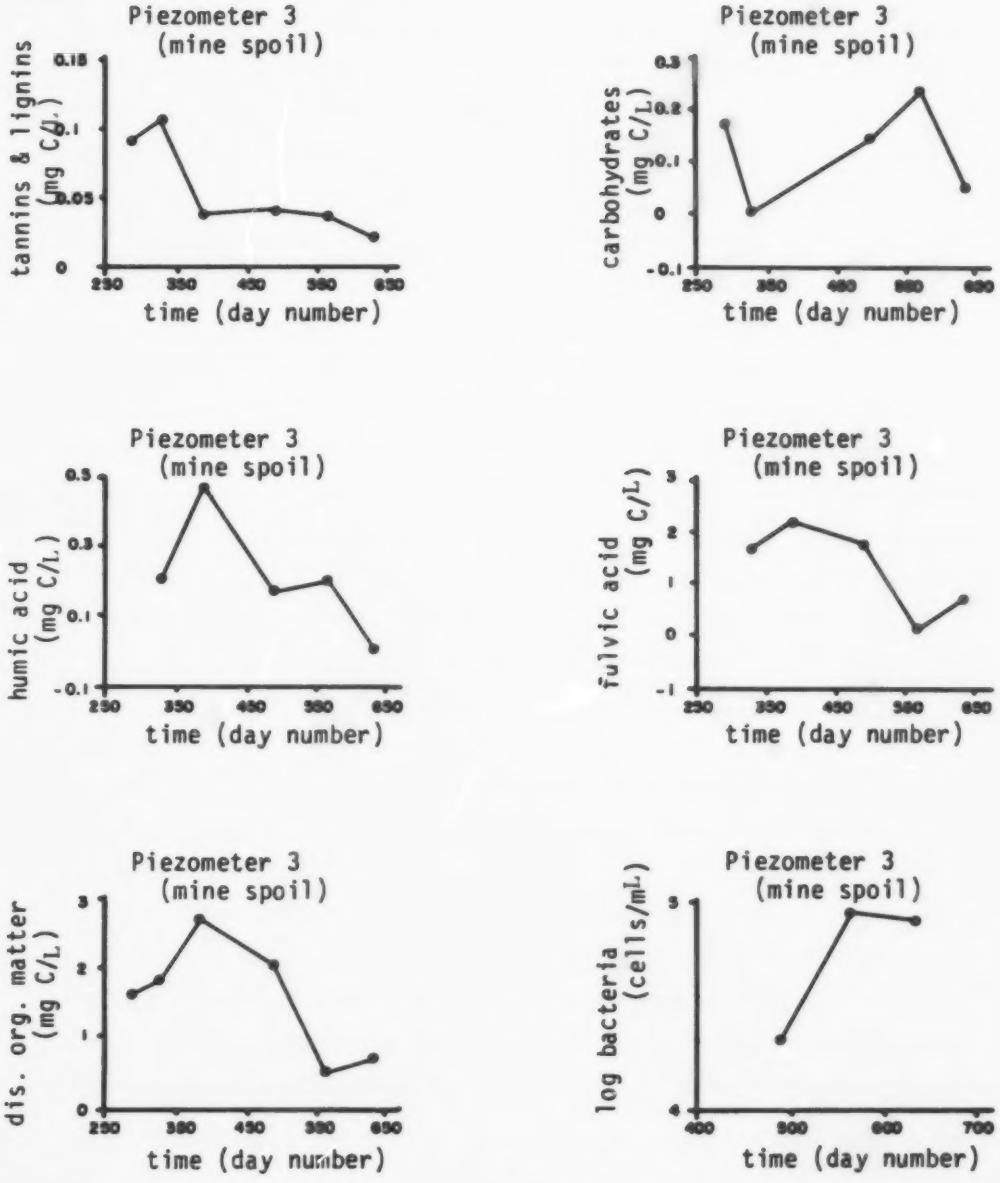
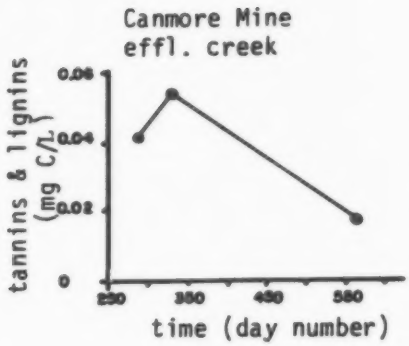
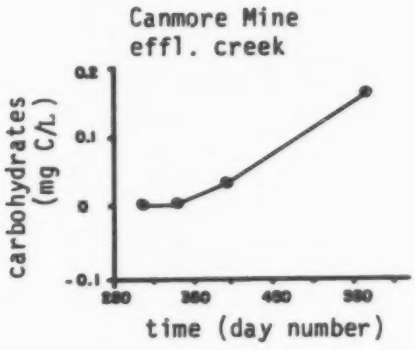
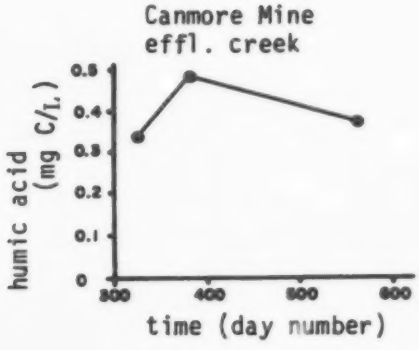
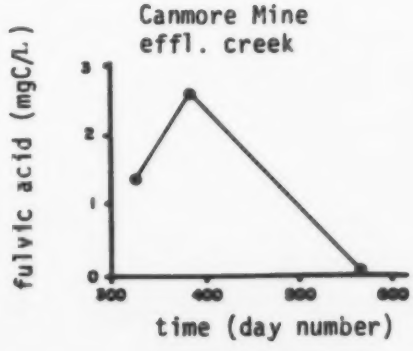


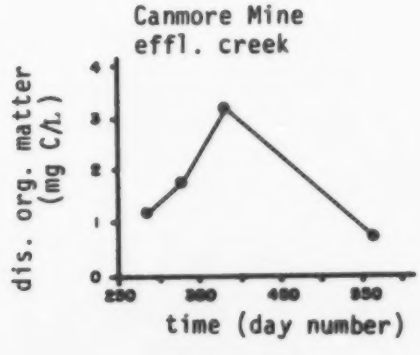
Figure 11. Concentrations of organic parameters measured over time at Canmore in the tributary to Canmoré Creek which drains the spoil bank expressed in milligrams of carbon per litre.











in the summer and fall than in the winter and spring. This may reflect the advent of peak groundwater levels which occur in the summer from infiltrated snowmelt. The concentrations of tannins and lignins are not very much different, but higher levels are found in the spoil piezometer (P3) than in the control piezometer (P1) or in Mine Effluent Creek (the mean values are reported in Table 19). These differences cannot be considered significantly.

2.2.1.2 Carbohydrates. Carbohydrates are very similar in concentration to tannins and lignins (Table 19). They tend to be more variable, ranging from 0.04 to 0.33 mg/L with an average value of 0.09 mg/L. An examination of Figures 9 to 11 reveals that they are highest in the summer and can be at levels below detection in the winter in both the spoil and control piezometers. Mine Effluent Creek showed a steady increase in the concentration of carbohydrates during the study period. At this site, carbohydrates were observed to increase while tannins and lignins were decreasing although this cannot be said for P1 or P3. Carbohydrates are known to be bound to humic substances but de Haan and de Boer (1978) have also shown that at least half of these bound sugars are only very weakly associated with large molecular weight compounds. The seasonal change in the concentration of carbohydrates may reflect some change in the nature of this association as well as the effects of microbial uptake.

2.2.1.3 Humic Acids. Humic acids are present at concentrations about half an order of magnitude greater than tannins and lignins or carbohydrates, ranging from 0.25 to 0.43 mg/L and averaging 0.32 mg/L expressed as carbon (Table 19). Concentrations were higher in the fall in P3 and Mine Effluent Creek but reached a seasonal peak in the summer in P1 (Control). A peak in concentration was observed for humic acid, tannins and lignins, and carbohydrates in the summer samples in the control piezometer (P1) as well. This was not observed to be the case in samples which had been in contact with mine spoil (Figures 9 to 11).

2.2.1.4 Fulvic Acids. Fulvic acids, which may include other organic molecules not identified as discussed previously, generally made up most of the dissolved organic matter present. The average concentration in all the installations was 1.23 mg/L expressed as carbon, and ranged from 0.83 to 1.6 mg/L. Seasonal peaks occurred in the winter in all three sampling sites described in Figures 9 to 11. This time period coincides with low groundwater levels and concentrations drop as far as zero (in Mine Effluent Creek) during high water periods in the early summer.

2.2.1.5 Dissolved Organic Matter. The seasonal behaviour of this parameter parallels fulvic acid, which makes up most of the dissolved organic matter. The average concentration was 1.35 mg/L ranging from 0.25 to 1.34 mg/L organic carbon. Although these values agree closely with other measurements made in the area (Wallis et al. in press), they are low in comparison with those found in natural waters in other areas of Canada (Lawrence 1978) The highest levels of dissolved organic matter were found in the winter, in contrast with carbohydrates. Seasonal dilution by snowmelt waters may be the controlling factor. As found by previous workers (Larson 1978, Lawrence 1978), dissolved organic matter is mostly made up of large molecular weight humic substances in surface and groundwaters. This is also in agreement with other work undertaken previously nearby in the Marmot Basin (Wallis et al. in press; Telang et al. 1976). This predominance is reflected in the chemical nature of coal itself.

2.2.1.6 Phenols. Simple phenols were measured on two occasions at Canmore in the fall of 1978. The concentration of phenols was below detection in all of the samples and the analytical procedure was tedious, so measurement of this parameter was discontinued. The 4-aminantipyrene method used only detects simple phenolic compounds. It is possible that a more sophisticated gas chromatographic technique would have detected more complex phenols although Campbell, Pellizzari, and Santor (1978) found only trace levels (0 to 2μ g/L) in a coal seam in Wyoming.

2.2.1.7 Amino Acids. Amino acids are present in groundwaters because they are leached from soil and decaying biological material. Their concentrations are depleted because of chemical and biological degradation so that at any one time the concentrations of individual amino acids depend upon both the source and the depletion processes which have occurred. The situation is further complicated because free amino acids may condense into proteins (combined) or combined amino acids may be hydrolyzed into free amino acids, particularly at low pH. The combined form, more properly called protein, is more resistant to chemical and biological attack because reactive sites are protected and molecular size is greatly increased. For this reason, they may be considered to be more representative of the original source than the free amino acids in the absence of polymerization.

Free and combined amino acids were measured at selected sampling sites in April 1979 and at all sampling sites in July 1979. The results from these analyses are reported in Figures 12 and 13 and the key to the amino acid numbers appears in Table 20. In April the total concentration of all amino acids averaged 130 µg/L in all of the groundwater samples (including spring water) but was much lower in Canmore Creek. This may be because of the more favourable environment for degradation in aerobic surface waters. The pattern of distribution of free and combined amino acids is similar in April, when the most prevalent amino acids, both free and combined, were proline, threonine, glutamic acid, aspartic acid, and glycine with the rest either not present at all or only at low and variable levels. At this time P1 (control), P2A (mine spoil), and P6 (mine spoil) showed very similar distributions of combined amino acids. The sample from Mine Effluent Creek was similar but most of the amino acids had disappeared in Canmore Creek below the confluence with Mine Effluent Creek, presumably because of dilution. The remaining amino acids, proline, threonine, aspartic acid, and glutamic acid, appear to be the most resistant to chemical or microbial degradation.

In July, free glycine and lysine were usually the most abundant amino acids in groundwater but not in surface waters. The other amino acids were low and variable and the total concentration

Table 20. Identification of amino acids by number which correspond to the x-axis of the graphs in Figures 12 and 13.

Number	Amino Acid
3	Alanine
4	Valine
5	Glycine
6	Isoleucine
7	Leucine
8	Proline
9	Threonine
10	Serine
11	Cysteine
12	Methionine
13	4-OH-Proline
14	Phenylalanine
15	Aspartic Acid
16	Glutamic Acid
17	Lysine
18	Tyrosine
19	Ornithine

Figure 12. Concentrations of amino acids found at selected sampling sites at Canmore on April 30, 1979. Results are reported in ug/l. The amino acids corresponding to the number on the x-axis are reported in Table 20.

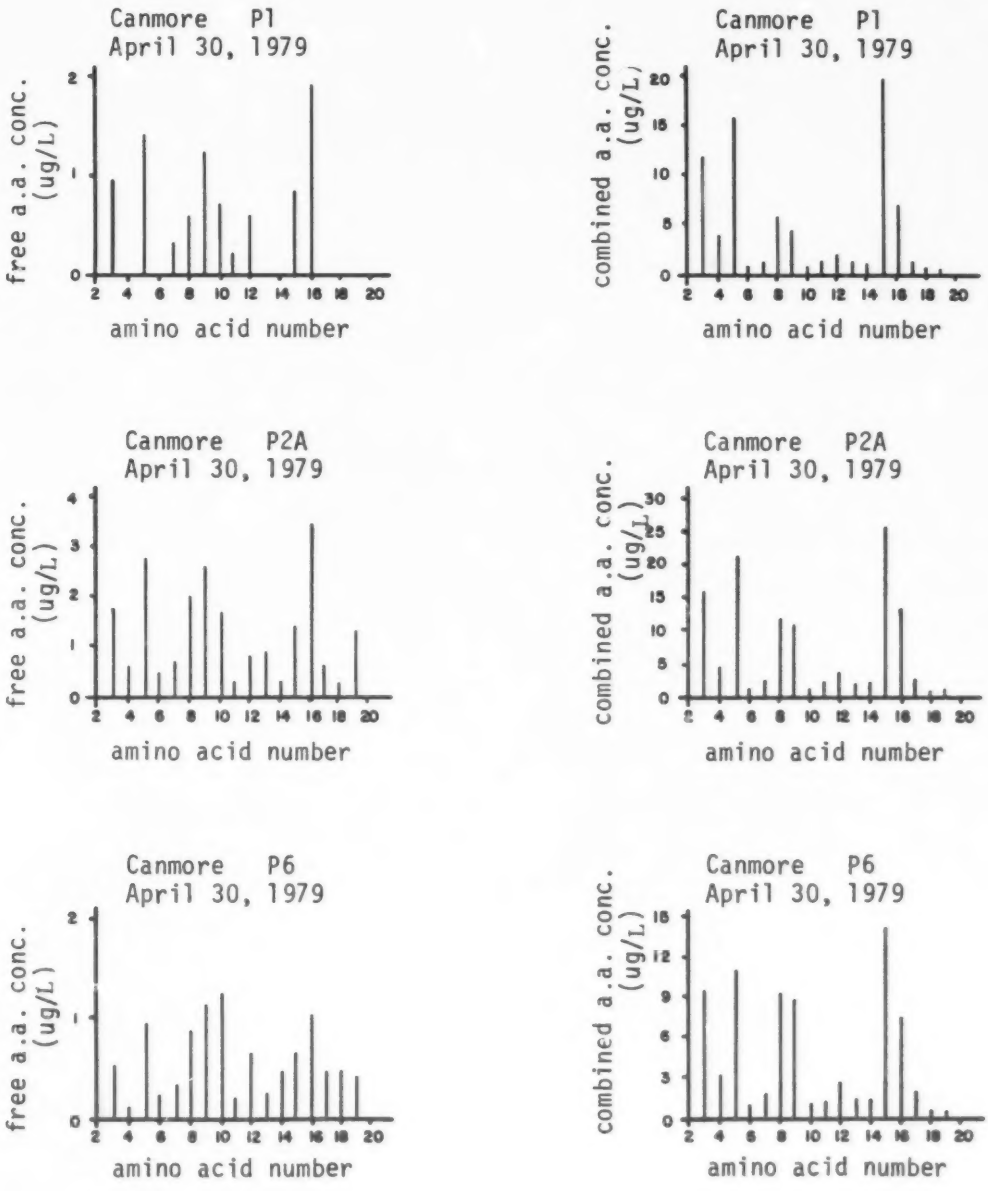
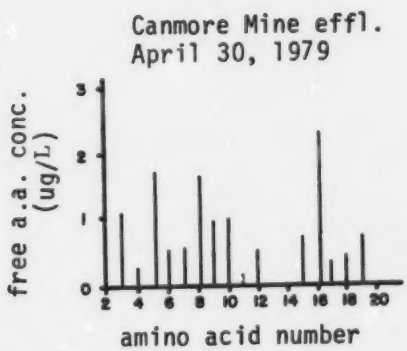
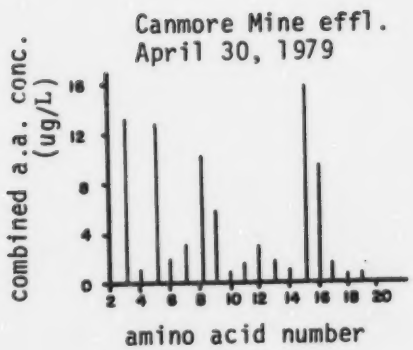


Figure 12. Concluded.





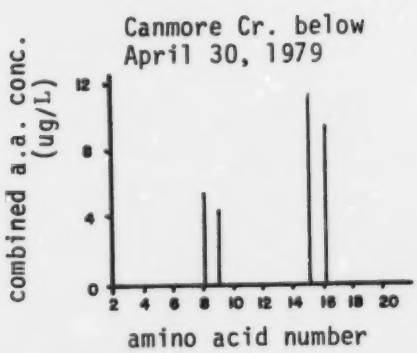


Figure 13. Concentrations of amino acids found at all sampling sites on July 17, 1979 at Canmore. Results are reported in ug/l. The amino acids corresponding to the number on the x-axis are reported in Table 20.

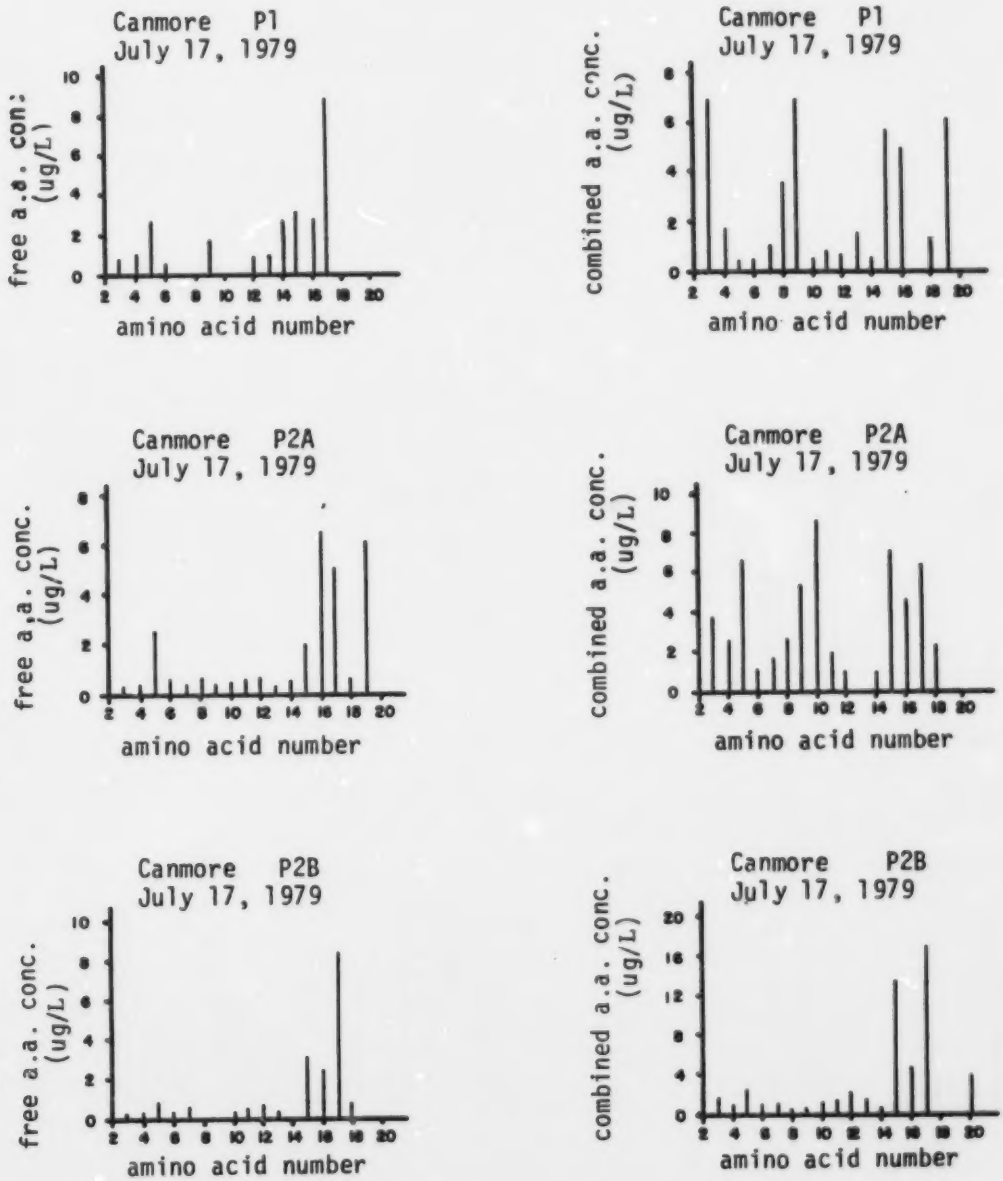
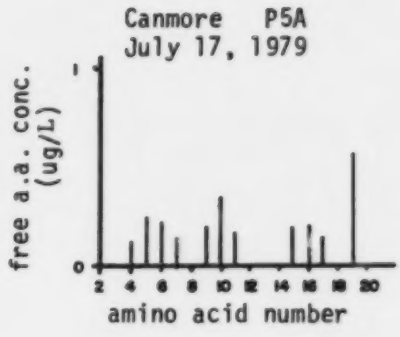
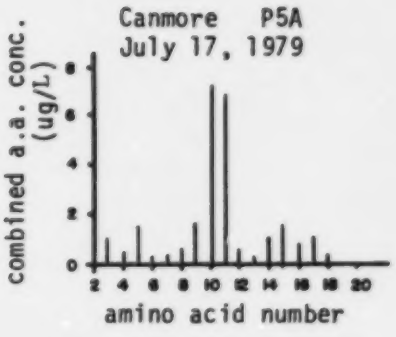
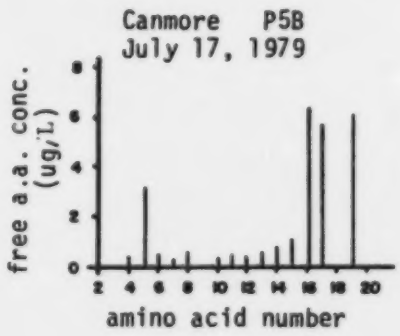
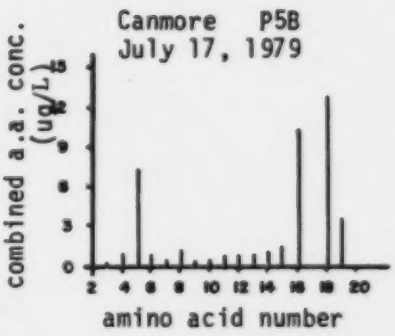


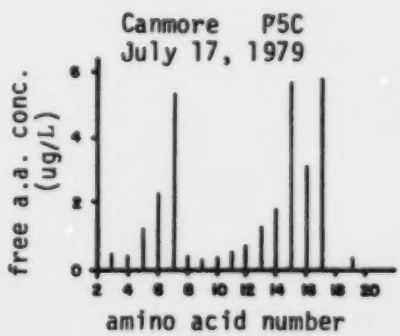
Figure 13. Continued.

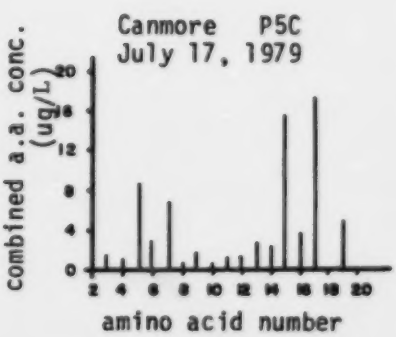












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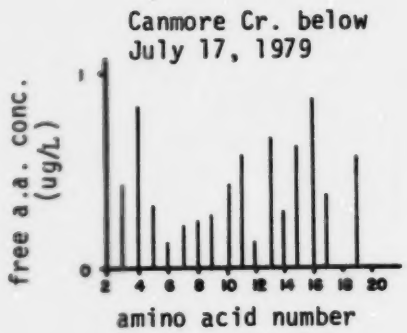

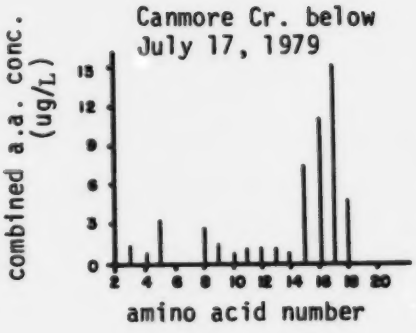

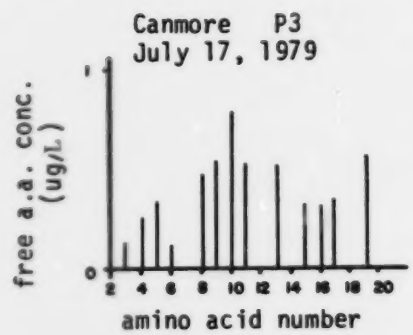

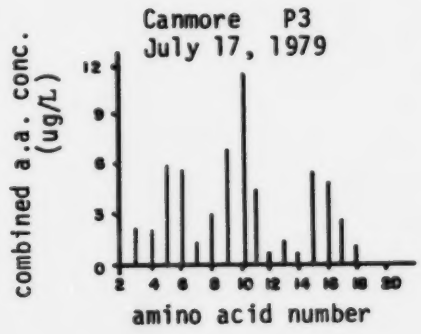

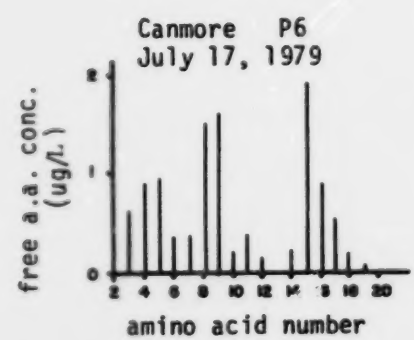

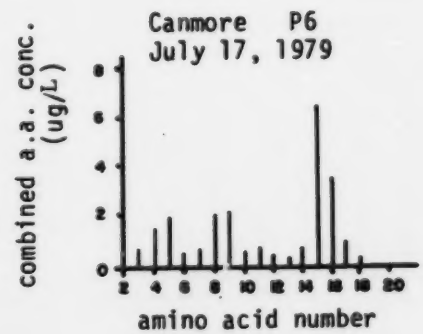

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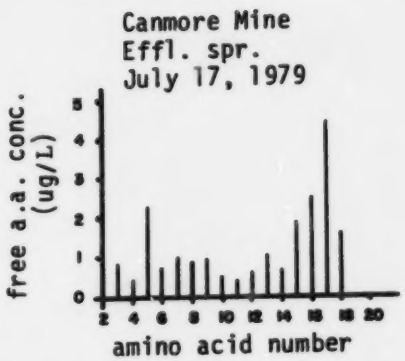

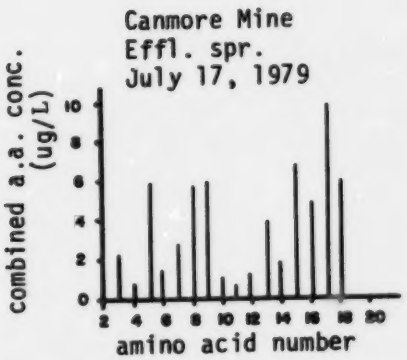

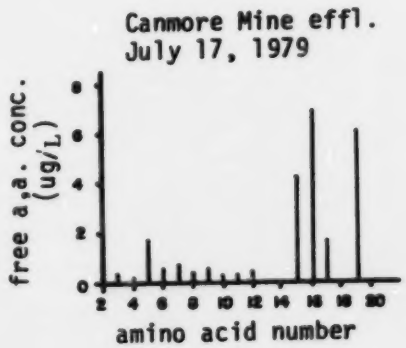

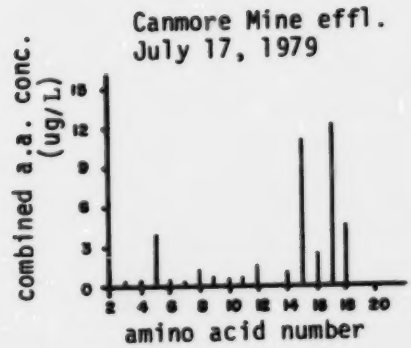

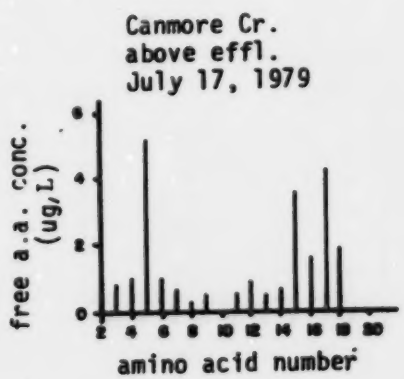

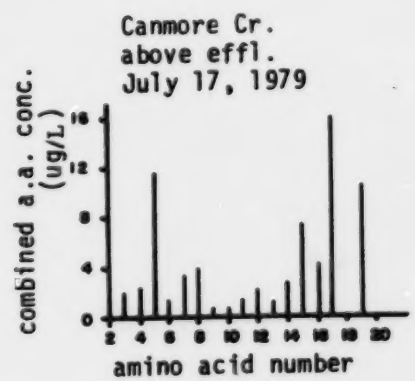

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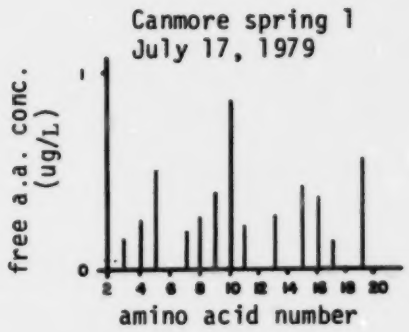
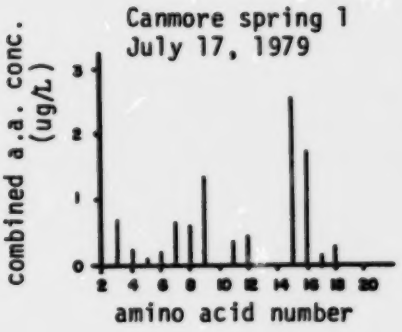
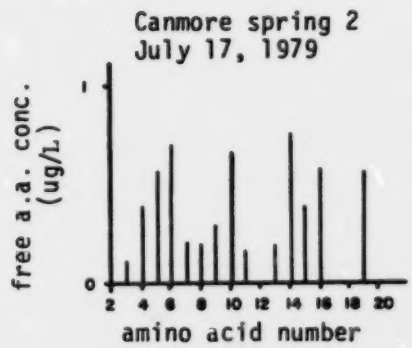
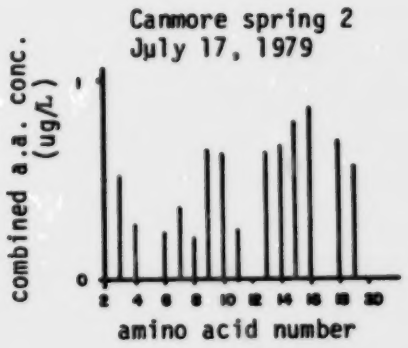
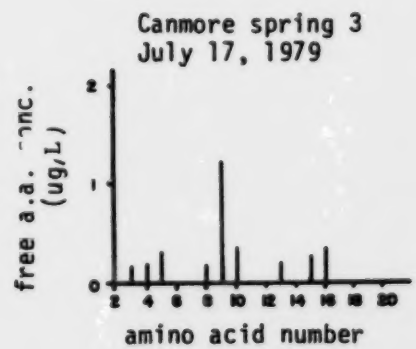
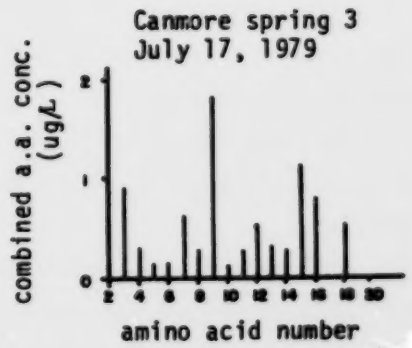












averaged 75 µg/L. The combined amino acids, aspartic acid and glutamic acid were always the highest while the rest were low and variable in concentration. No similarities between sampling sites were detected in either free or combined amino acids in July. The concentrations found were lower in July than in April, in keeping with the findings of Telang et al. (1976) in the Marmot Basin. Groundwater contains about an order of magnitude more amino acids than were found in the surface waters of the Marmot Basin study. That study classified amino acids into three groups as follows:

Group I Little or no change in loading throughout the seasons including alanine, glutamic acid, and ornithine;

Group II Strongly depleted in the fall season comprising aspartic acid, leucine, lysine, proline, serine and threonine; and

Group III Miscellaneous loading patterns comprising glycine, isoleucine, phenylalanine, and valine.

Although the data collected for this study were not sufficient to calculate mass loading effects as in the Marmot study (because of the difficulty of accurately calculating mass groundwater movement), the concentration data presented in Figures 12 and 13 suggest that different amino acids are the most stable. In both April and July aspartic acid and glutamic acid are the most stable and abundant amino acids. Others, such as ornithine, were never found in relatively high amounts although the Marmot data indicate that ornithine is stable in surface waters. The data for glutamic acid agree but aspartic acid should have been more strongly depleted. Considerably more work would have to be done to confirm any differences between surface and groundwaters. The variability obvserved in these data suggest that most amino acids, either combined or free, are undergoing transformations on a seasonal basis which are difficult to characterize.

The process of degradation may definitely be observed at Site 5 (piezometers 5A, 5B, and 5C) adjacent to the pond. In July, hydrological measurements indicated that water was being recharged from the pond so that water was moving from P5C to P5A. An examination of these data in Figure 13 shows that free amino acids were

strongly depleted by the time water reached P5A (note the concentration change on the y-axis for P5A). At the same time, the distribution of amino acids in the combined form changed from a dominance of aspartic acid and lysine to one of serine and cysteine. The source of the latter two amino acids is not evident from the free amino acid data so it is assumed that other transformations took place in the soil, perhaps involving coal and other solid organic material. It is also possible that interactions occurred with dissolved humic materials (de Haan and de Boer 1978).

As these compounds are actively taken up by a variety of microorganisms, and microbial populations are high (about 10^6 cells/mL in groundwater), the amino acids detected probably represented a "standing crop" undergoing fairly rapid transformation. It is suggested on the basis of these data that amino acids are more abundant in groundwaters than in surface waters and that they form a nutrient source for microorganisms. Amino acids are known to be associated with humic substances (de Haan and de Boer 1978) but the relation between chemical and biological interactions is not known.

2.2.2 Organic Chemical Changes Through a Cross-Section at Canmore

In order to detect changes in the concentration of organic parameters as groundwater passed from the forest edge through the mine spoil, the piezometers were originally installed in a cross-section from upstream to downstream. The results are reported in Figures 14 to 18 and these include a breakdown of seasonal changes for each papameter. The trend of the results is summarized in Table 21 in the same manner. Table 21 also contains a key equating the cross-section piezometer numbers used in Figures 14 to 18 with the piezometer identification numbers used in the map in Figure 2.

Tannins and lignins increased in concentration from the control piezometer (P1) through the mine spoil at all times of the year except January when they remained the same and in July when they went down. Carbohydrates were unchanged from fall through to spring, and decreased in July. Humic and fulvic acids remained the same at all times of the year except the summer when they decreased. Dissolved organic matter followed the same pattern as humic and fulvic acids.

Table 21. Changes in the concentrations of organic parameters on a seasonal basis as groundwater passes through spoil material from the forest edge at Canmore.

Organic Parameter	October	November	January	April	July	September
Tannins and Lignins	up	up	same	up	down	up
Carbohydrates	same	same	up	up	down	up
Humic Acid	--	same	same	same	down	same
Fulvic Acid	--	same	same	same	down	same
Dissolved Organic Matter	same	same	same	same	down	same

Key to piezometer installations used in the cross-section data presented in Figures 14-18.

Cross-Section Piezometer Number	Installation
1	P1 (Control)
2	P5A (Mine Spoil)
2.1	P5B (Mine Spoil)
2.2	P5C (Mine Spoil)
3	P2A (Mine Spoil)
3.1	P2B (Mine Spoil)
4	P3 (Mine Spoil)
5	Mine Effluent Creek

Figure 14. Tannins and Lignins sampled from installations in a Cross-Section through the Canmore Mine Reclamation Site 2. All concentrations in mg/l as organic carbon.

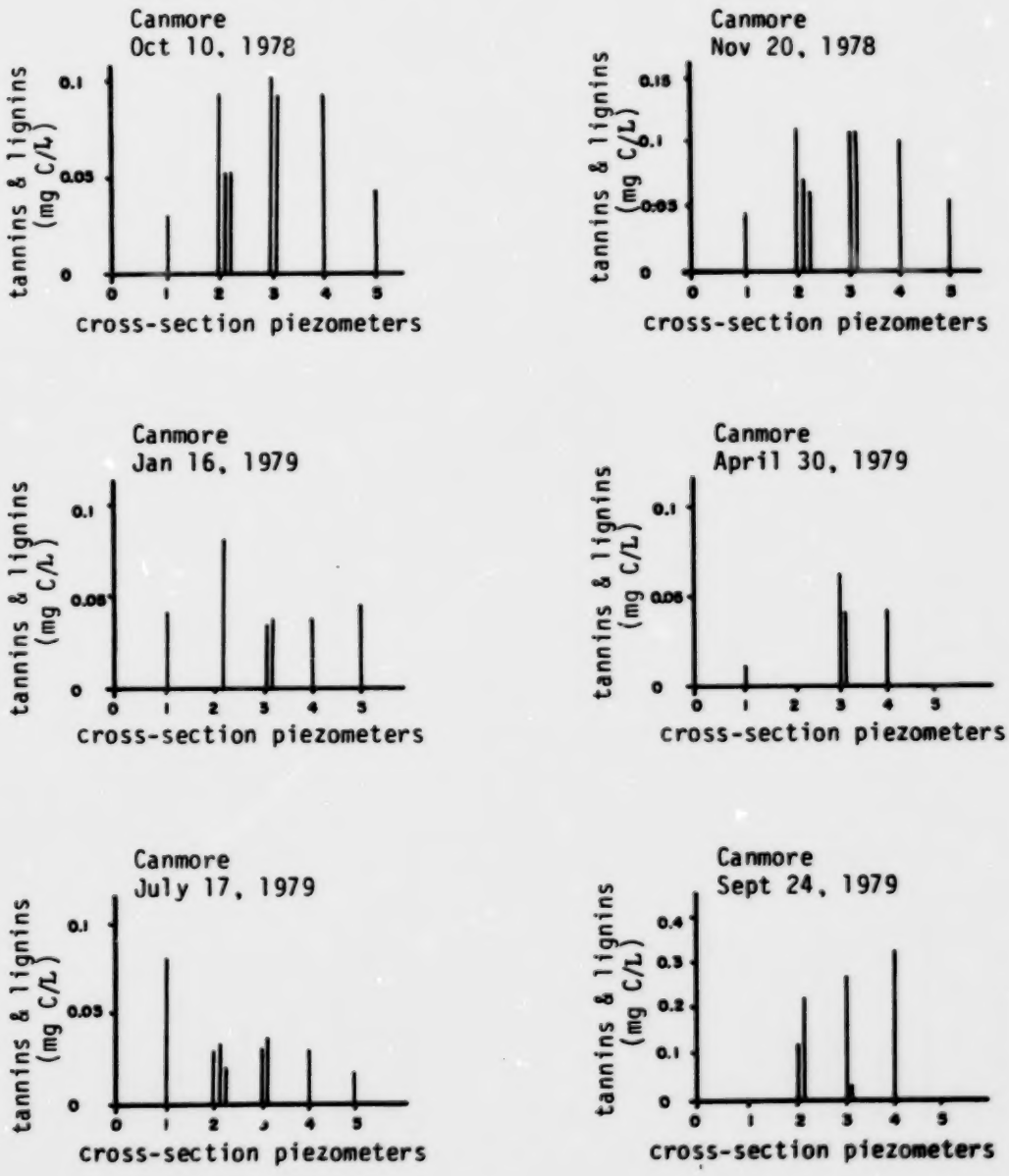


Figure 15. Carbohydrates sampled from installations in a Cross-Section through the Canmore Mine Reclamation Site 2. All concentrations in mg/l as organic carbon.

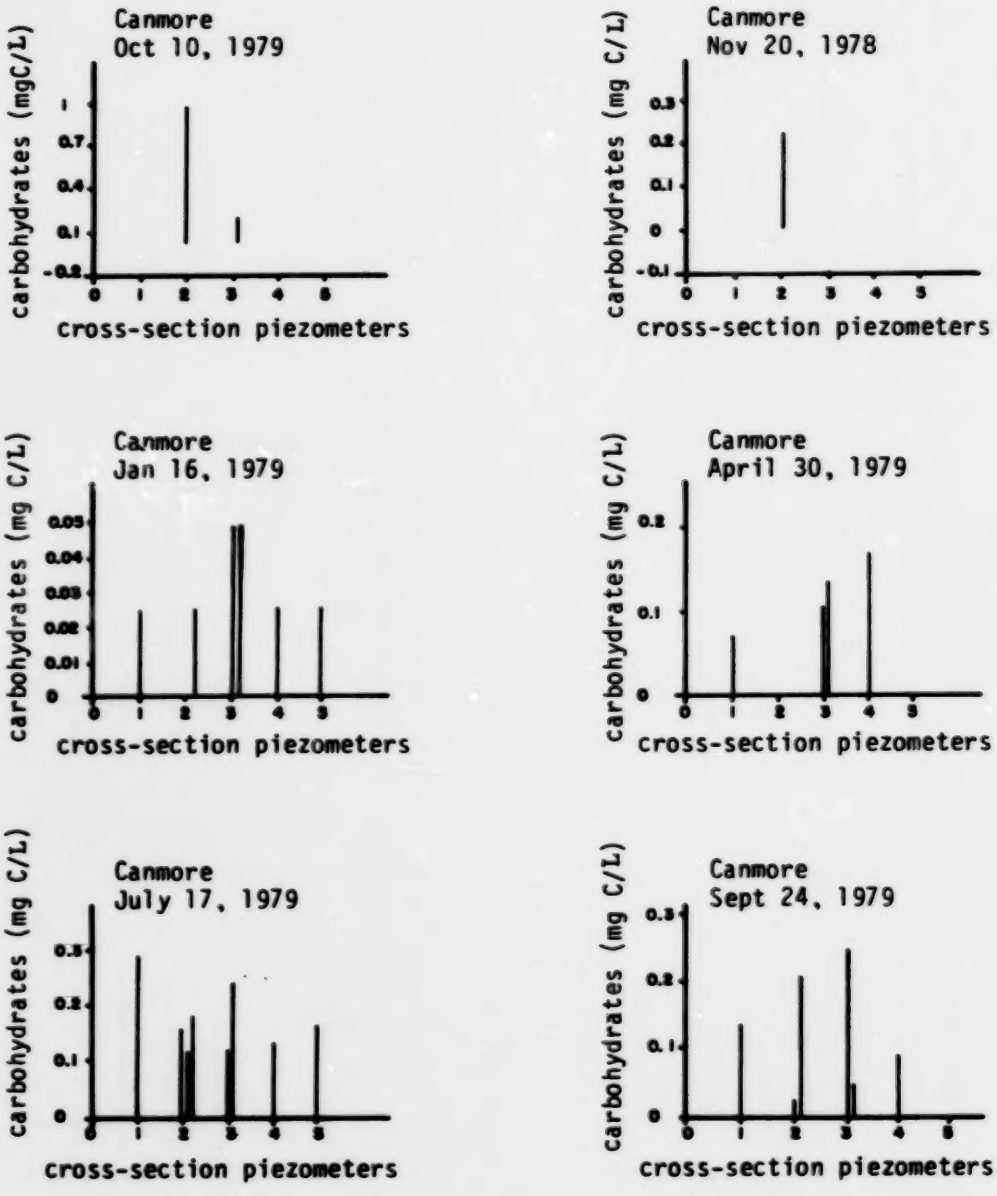


Figure 16. Humic Acids sampled from installations in a Cross-Section through the Canmore Mine Reclamation Site 2. All concentrations in mg/l as organic carbon.

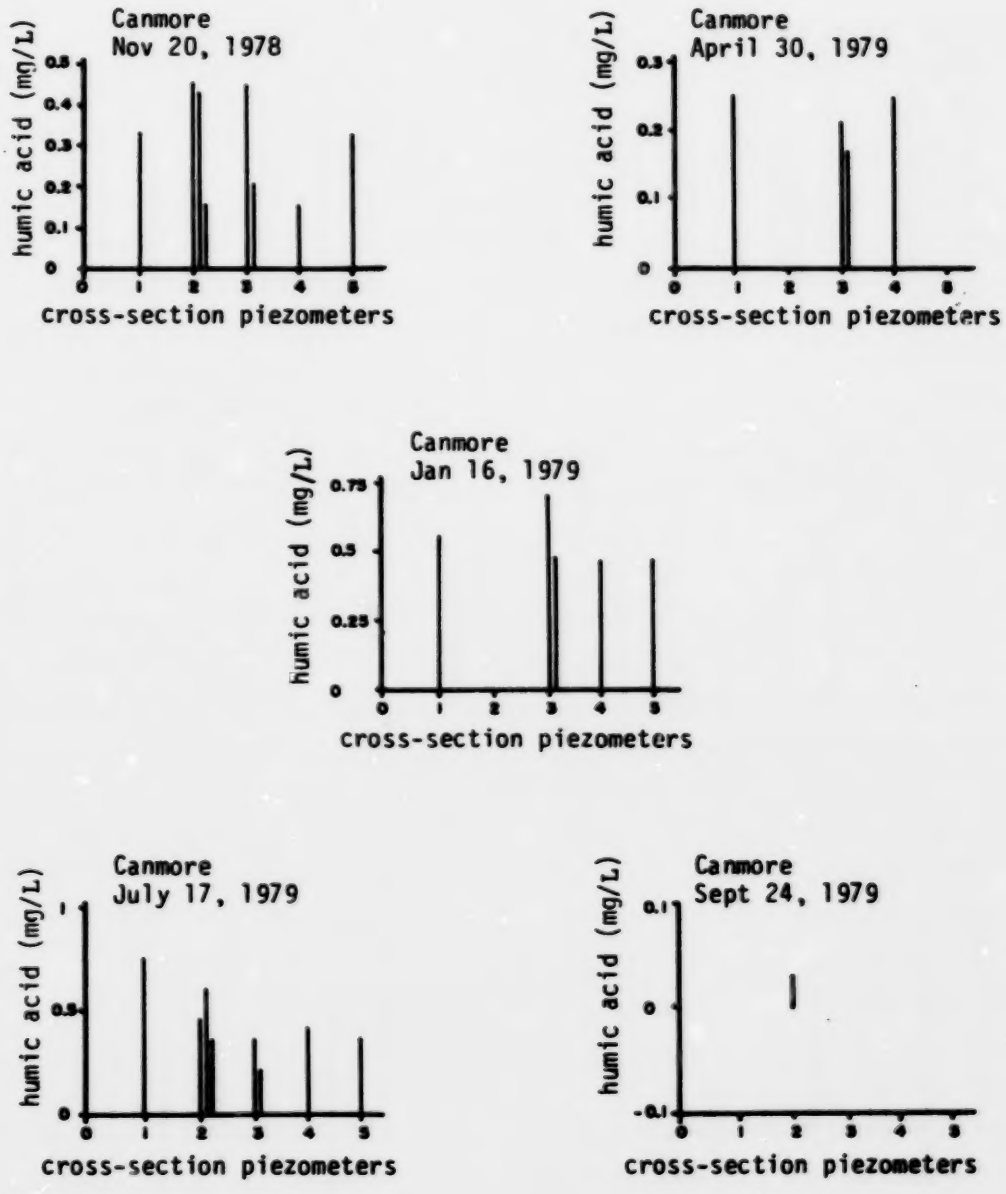


Figure 17. Fulvic acids sampled from installations in a Cross-Section through the Canmore Mine Reclamation Site 2. All concentrations in mg/l as organic carbon.

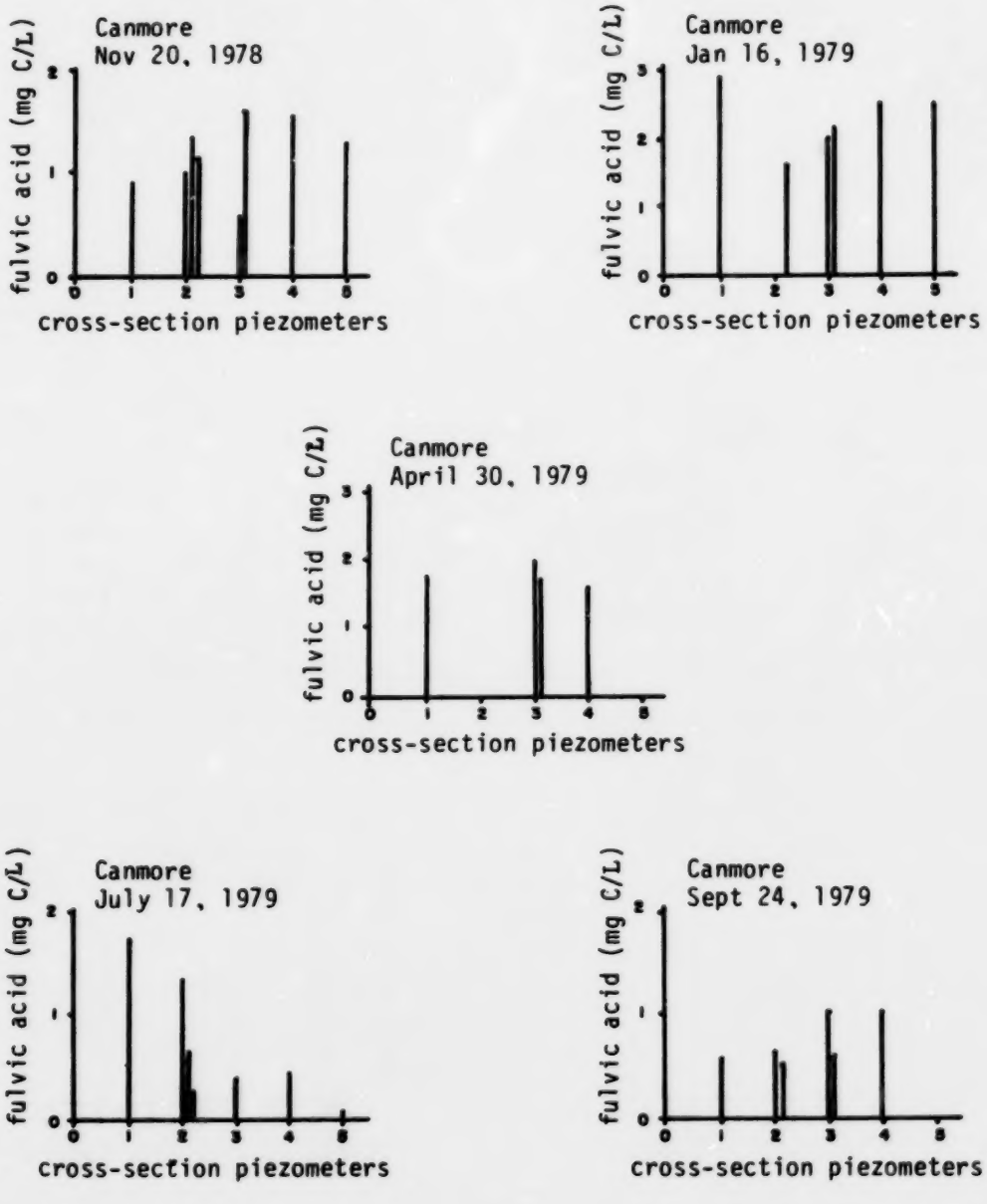
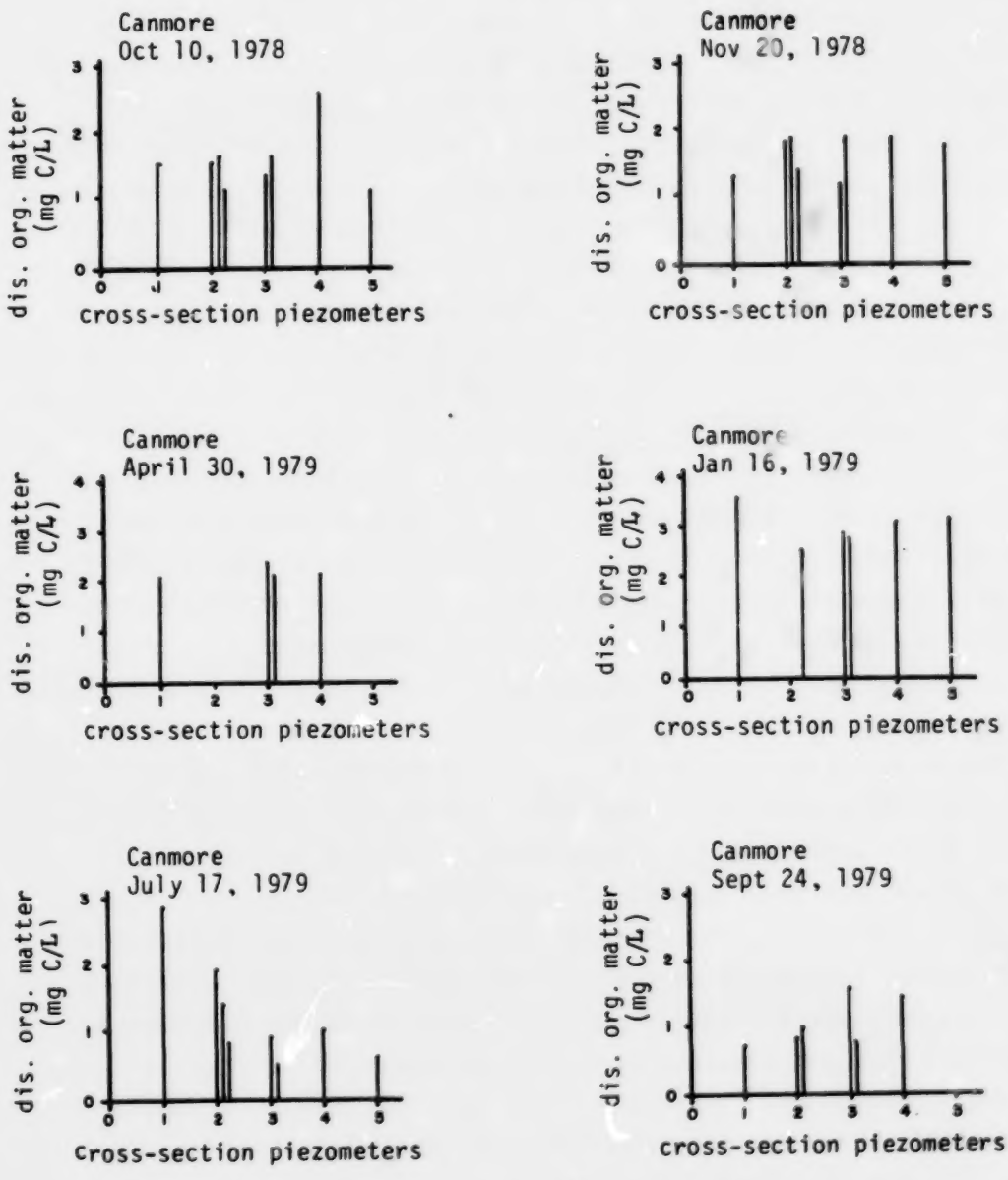


Figure 18. Dissolved Organic Matter sampled from installations in a Cross-Section through the Canmore Mine Reclamation Site 2. All concentrations in mg/l as organic carbon.



The most striking result from these data is the general decrease in concentration in the July sample for all organic parameters measured. A few increases were observed but the rest of the data indicate that no net changes occurred throughout most of the year in the mine spoil. It would be tempting to conclude that the dilution effect of the spring runoff alone is responsible for the July decrease and that these parameters are conservative, but an examination of Figures 14 to 18 shows that concentrations of all parameters are almost always much lower in the Mine Effluent Creek. This sampling site is actually a groundwater seep and should be no different from the piezometers in the nearby mine spoil. If these organic parameters are truly conservative, there should be no change in concentration between the spring and the groundwater. As this is not the case, it is suggested that seasonal transformation processes are also taking place through the mine site. This hypothesis is tested in Chapter 4 and the implications for inorganic chemistry are discussed.

2.2.3 Wabamun - General Results

A great many more wells and piezometers were available at Wabamun so the treatment of the data was somewhat different than those from Canmore. Initially, relationships were sought between the various organic parameters using all of the data collected from all installations. As found at Canmore, dissolved organic matter was strongly related to fulvic acid ($r = 0.97$) and weakly related to humic acid ($r = 0.43$). No other relationships could be detected between any other organic classes of compounds measured. As discussed previously, the strong relationship between dissolved organic matter and fulvic acid is most probably because of the analytical techniques used.

Tannins and lignins were found at an average concentration of 0.09 mg/L ranging from 0 to 0.5 mg/L at Wabamun, only slightly more than the concentrations found at Canmore. Carbohydrates were present at higher concentrations with an average of 0.22 mg/L ranging from 0 to 2 mg/L. This represents nearly half an order of magnitude difference in concentration between Wabamun and Canmore. As carbohydrates are important nutrient sources for microorganisms,

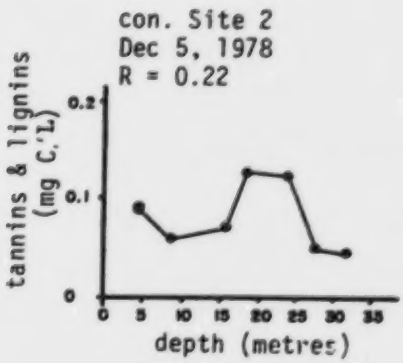
this difference is important. Humic acids were measured and found to be at an average concentration of 0.49 mg/L ranging from 0 to 1.8 mg/L compared with an average of 0.32 mg/L and a range of 0.25 to 0.42 mg/L at Canmore. Fulvic acid averaged 2.72 mg/L at Wabamun and ranged from 0 to 8 mg/L, considerable higher than at Canmore (average 1.23; range 0.83 to 1.6 mg/L). Dissolved organic matter was also higher, ranging from 0.5 to 9.7 mg/L and averaging 3.57 mg/L. Phenols were too low to measure.

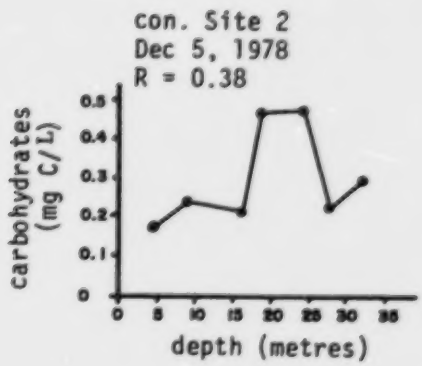
2.2.4 Relations Between Organic Parameters and Depth Inside and Outside the Wabamun Mine

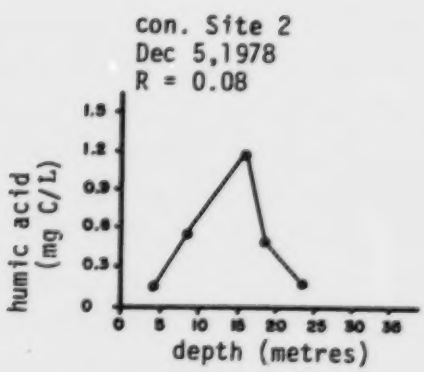
The concentrations of all organic parameters measured on a regular basis are plotted against installation depth in Figures 19 to 23 for five different sampling dates over one year. Each figure includes data from Control Site 2 and one or two installation sites within the mine. The deepest installation is the 10 cm well drilled into the bedrock below the spoil and the shallower installations are 5 cm piezometers completed in the spoil material at various depths. The organic drilling mud Revert was used at all nest sites inside and outside the mine. Most of these wells were drilled over one year before samples were taken for this project and no obvious contamination can be observed in the organic chemical data discussed below. As all sites were equally affected, the comparisons made are considered valid. A detailed discussion of the possible effects of Revert upon organic and inorganic groundwater chemistry is discussed in Section 2.3.

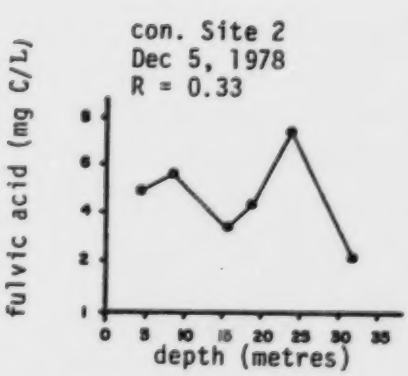
In Figure 19, the distribution of the organic compounds measured with depth is presented for December 5, 1978 at Sites 1 and 2 and at Control Site 2. The regression coefficient, r, also appears on each graph. At Control Site 2, no obvious relationship with depth can be distinguished for any parameter when all the data are considered. Maximum concentrations of all parameters were found between depths of 17 and 27 m. With the exceptions of these maxima, a very gradual trend towards decreasing concentration with depth may be observed. It is possible that infiltration with Revert may be responsible for these increases in concentration, but this will be discussed in the next section. At Site 1, no obvious trend was

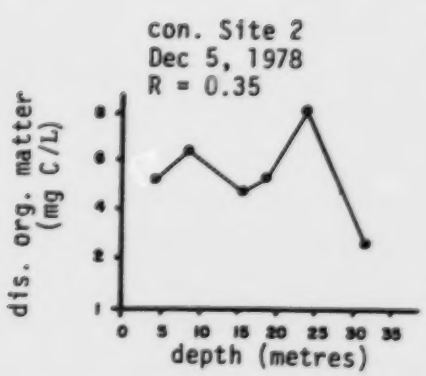
Figure 19. Relationships between organic parameters and depth inside and outside the Wabamun Mine - Dec. 5, 1978.











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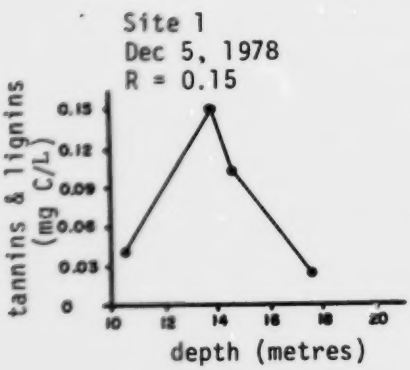

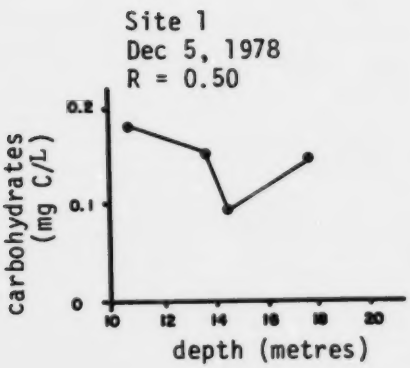

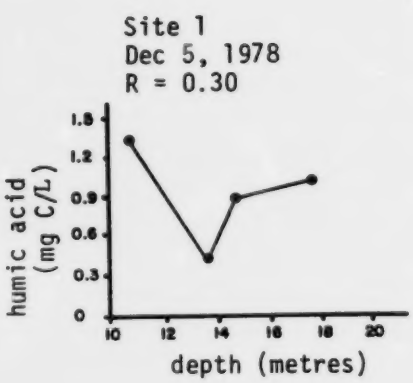

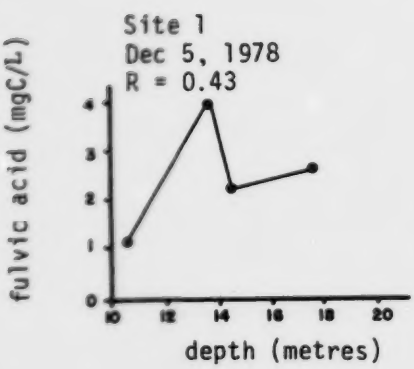

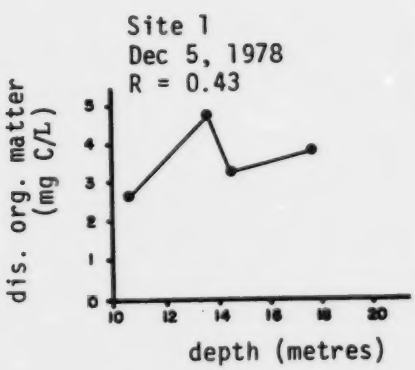

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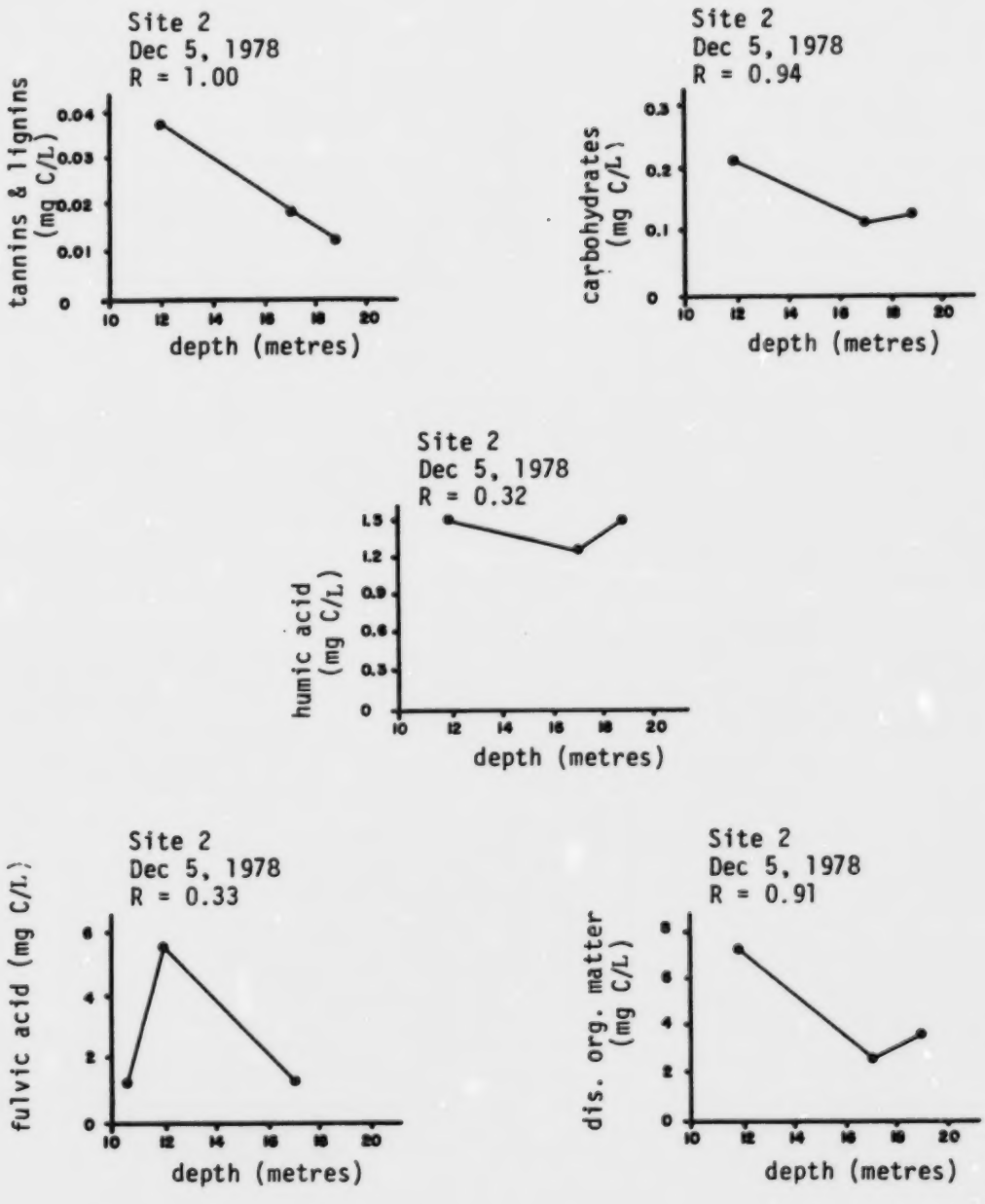
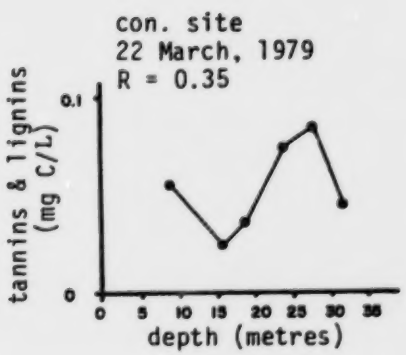
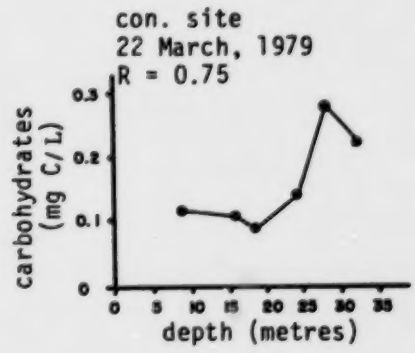
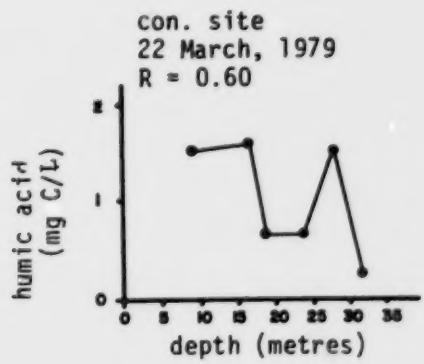
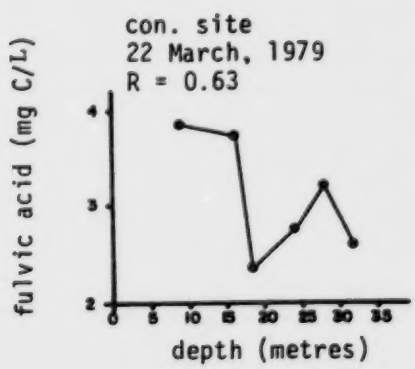


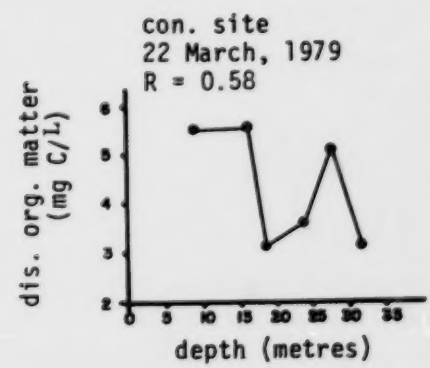
Figure 20. Relationships between organic parameters and depth inside and outside the Wabamun mine. -March 22, 1979.











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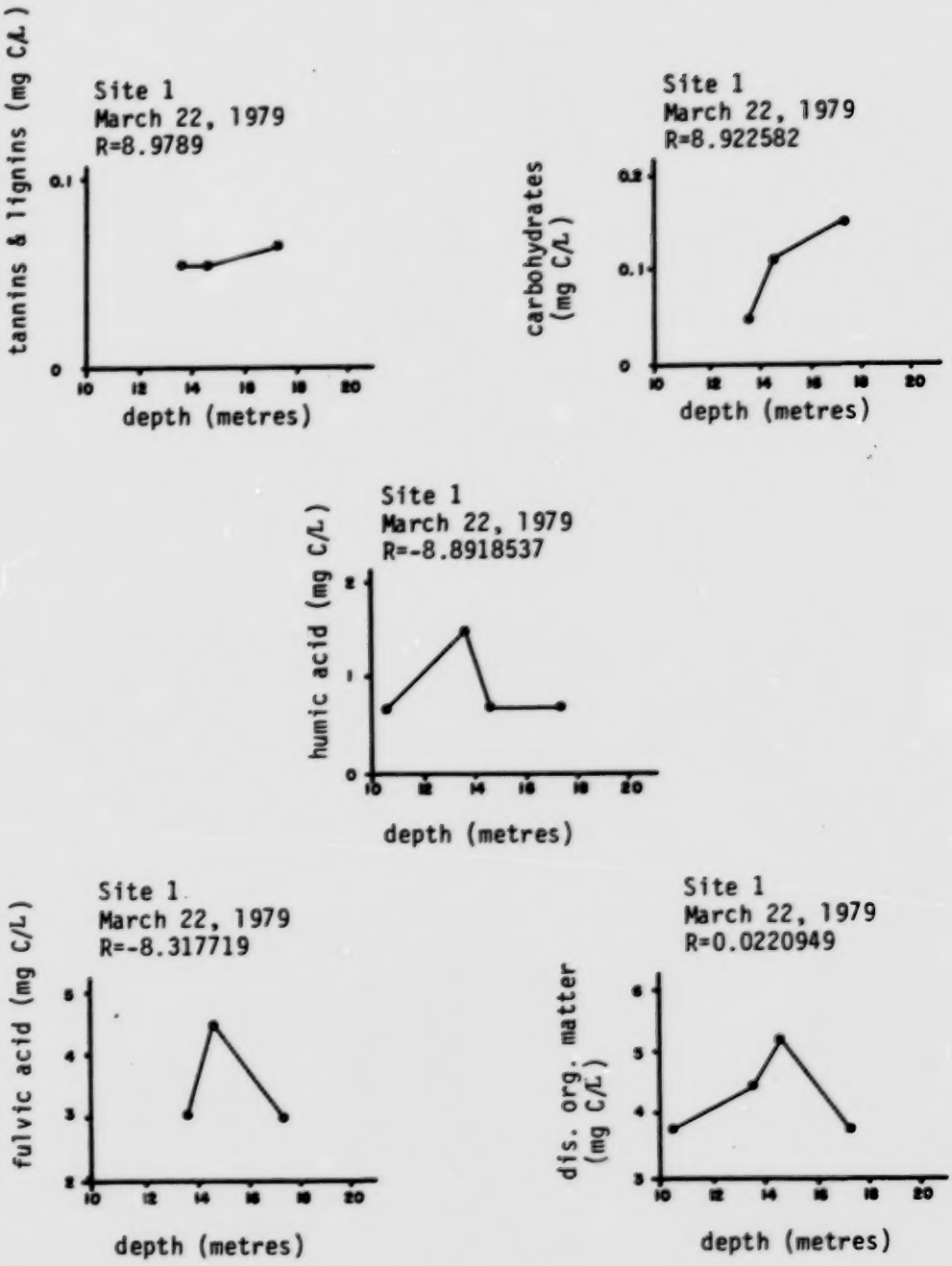

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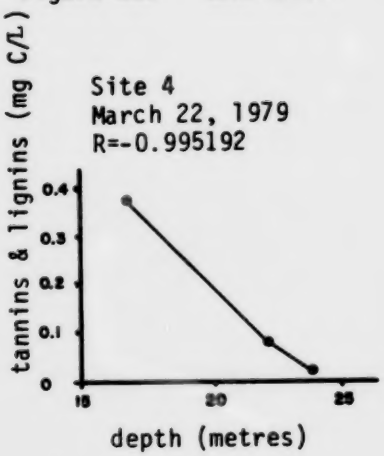
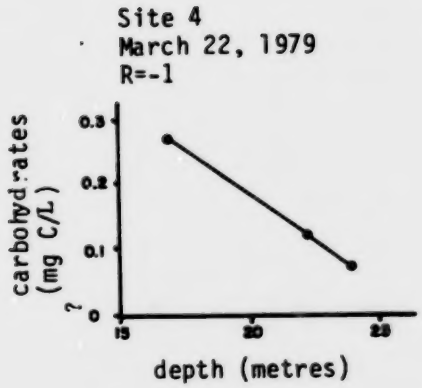
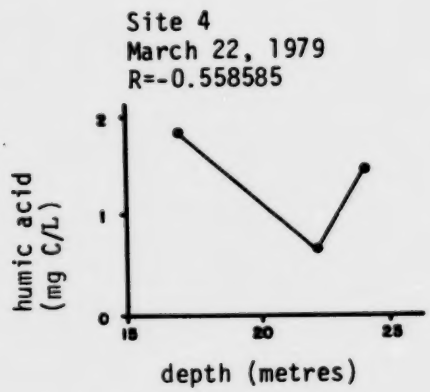
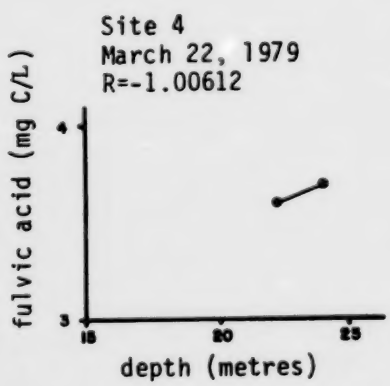








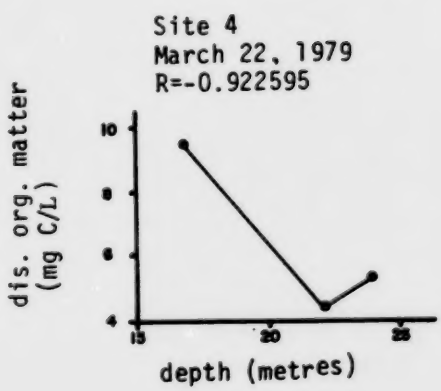
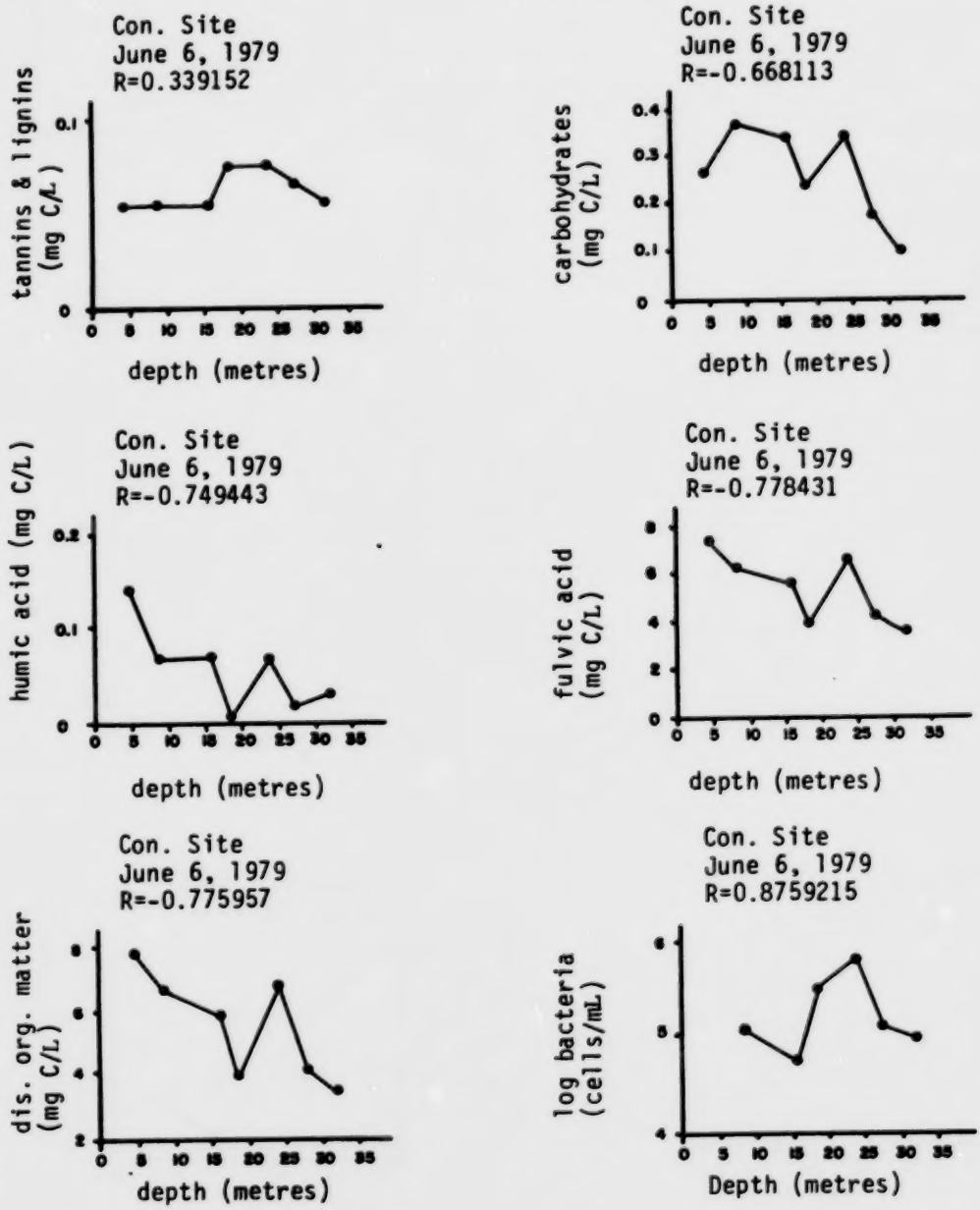


Figure 21. Relationships between organic parameters and depth inside and outside the Wabamun Mine - June 6, 1979.



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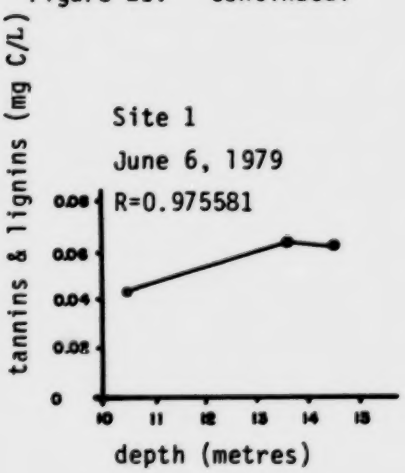

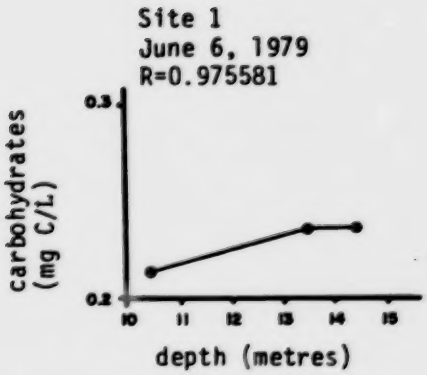

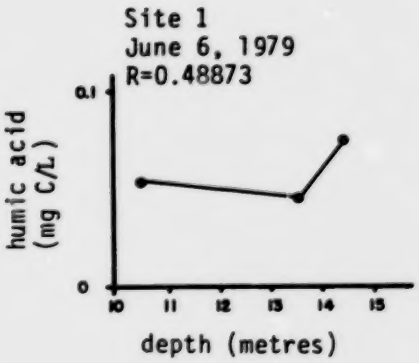

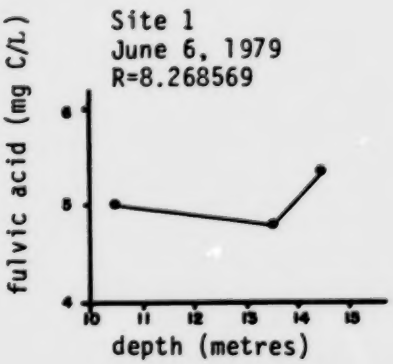

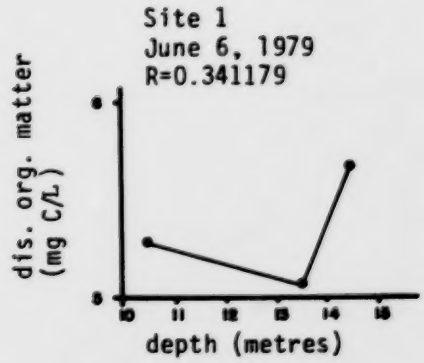

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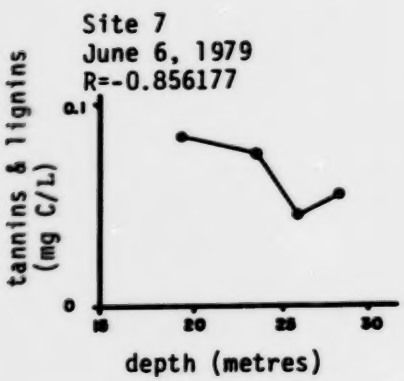
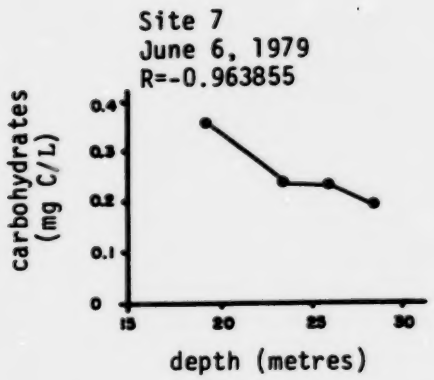
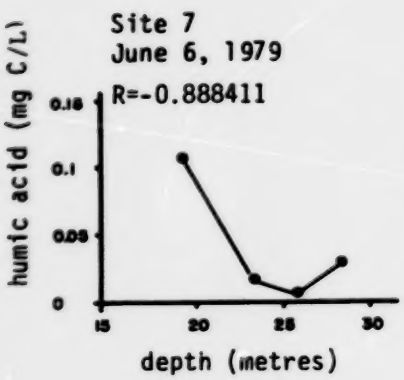
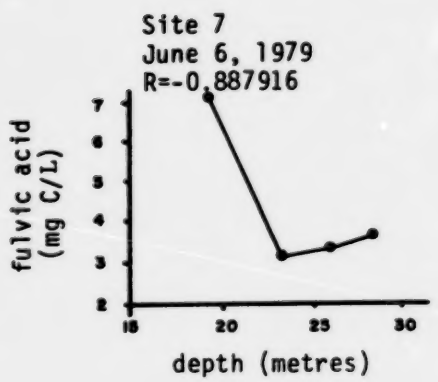
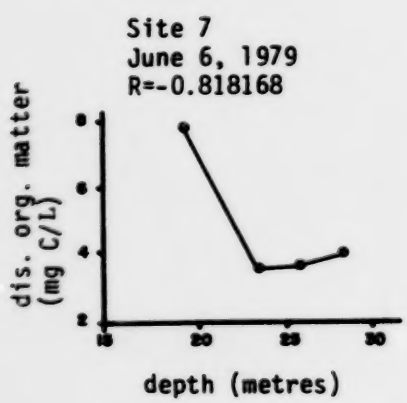










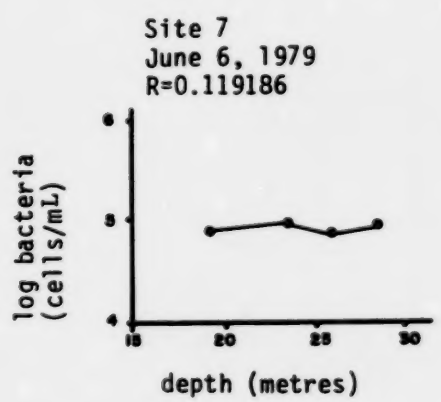
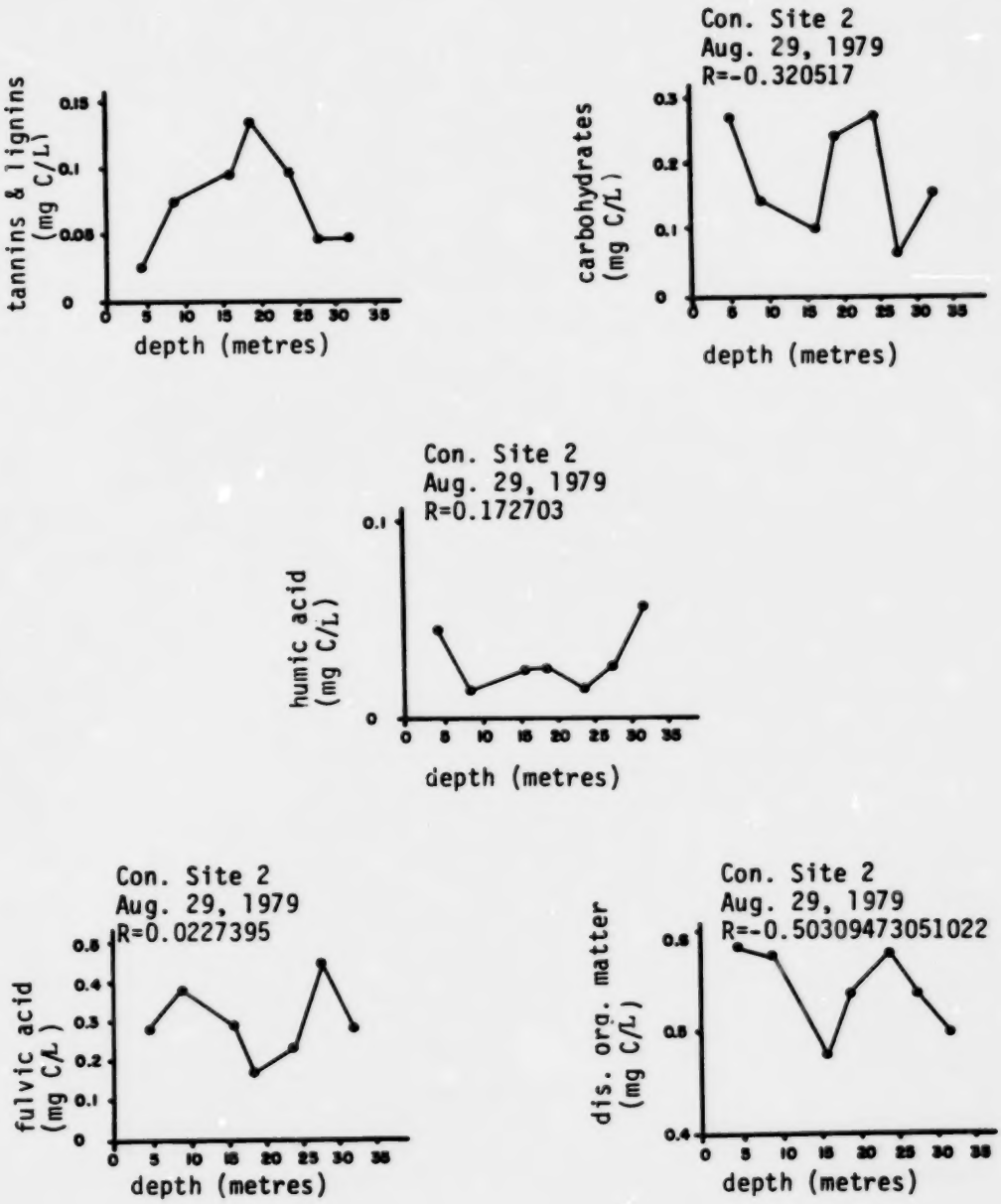


Figure 22. Relationship between organic parameters and depth inside and outside the Wabamun Mine - August 29, 1979.



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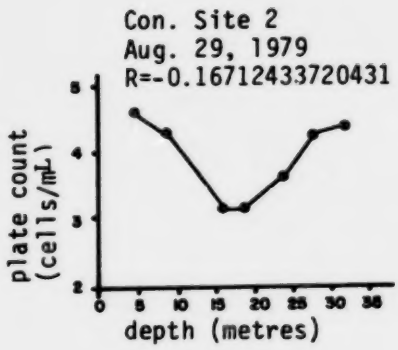

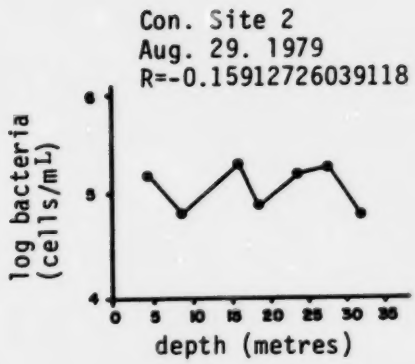

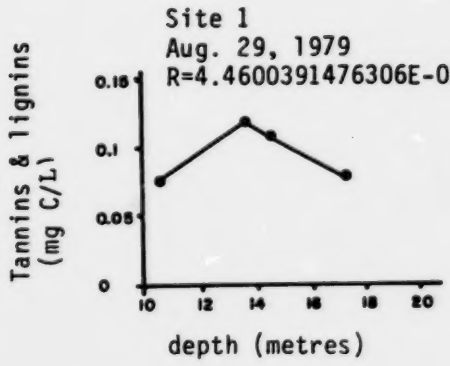

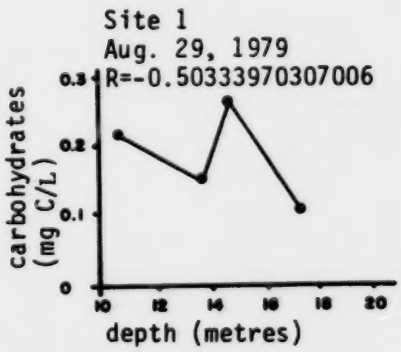

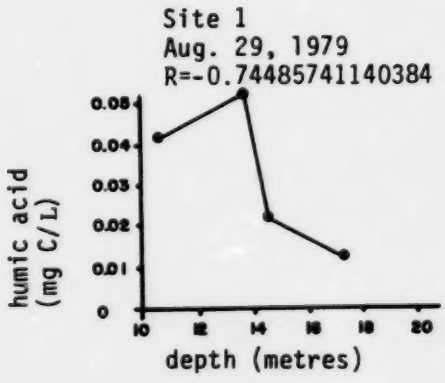

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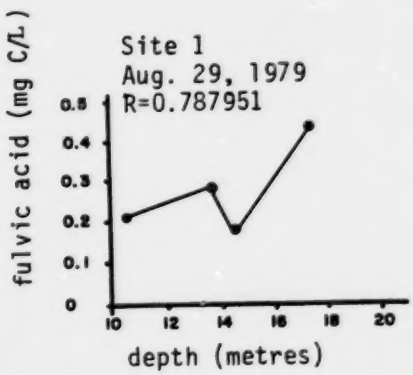

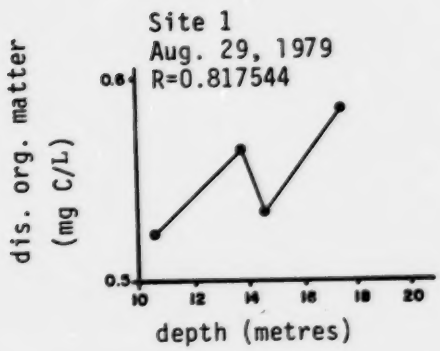

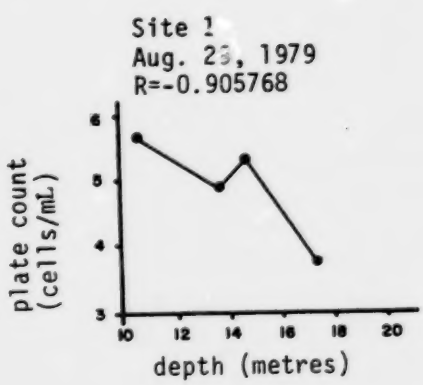

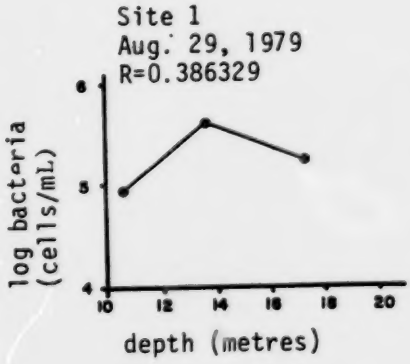

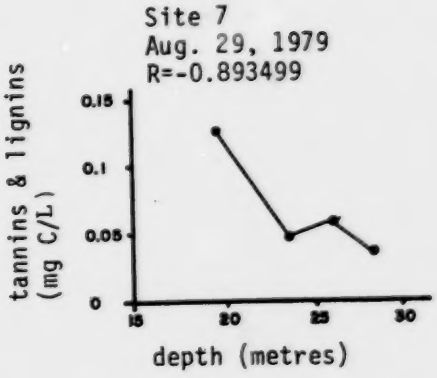

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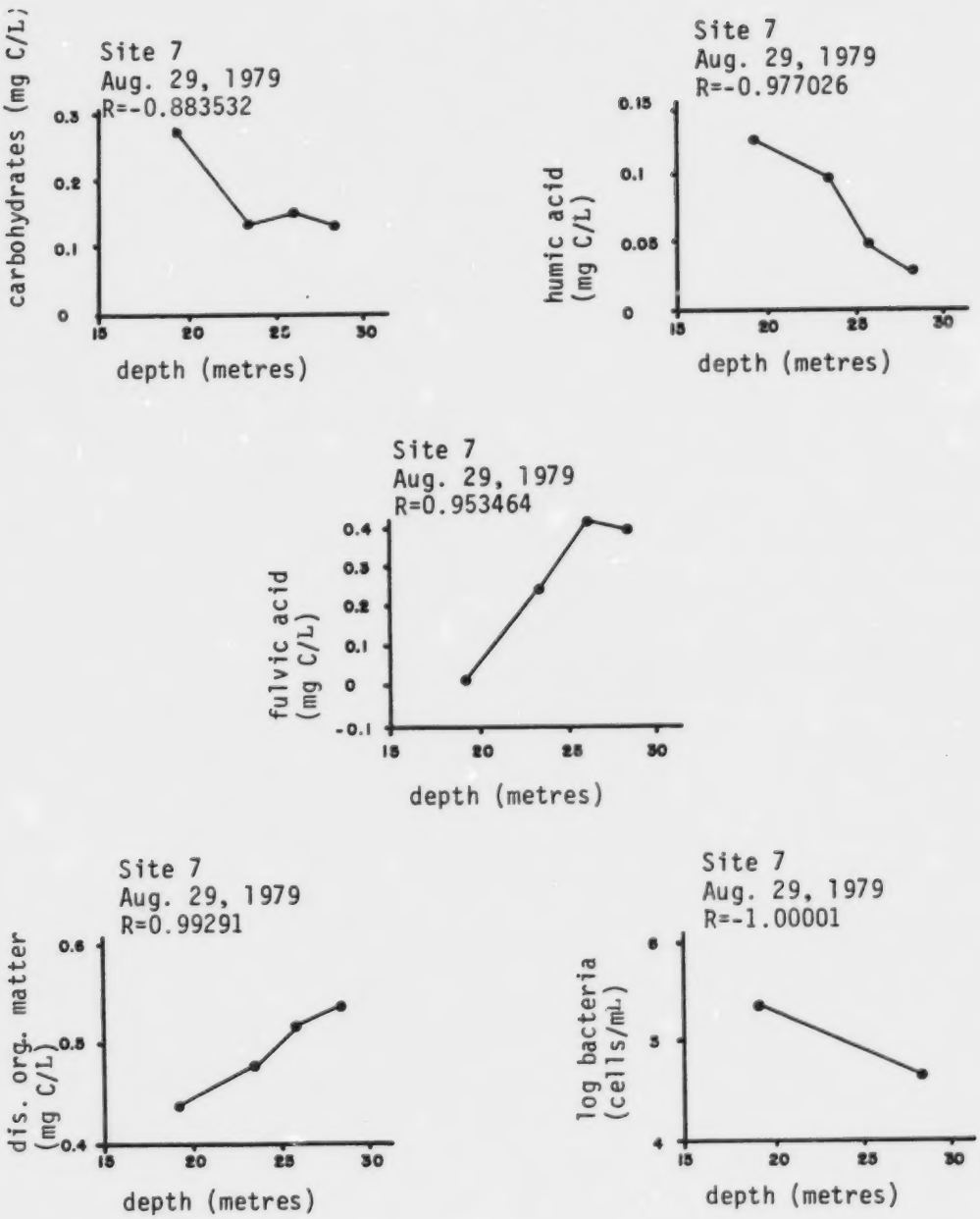
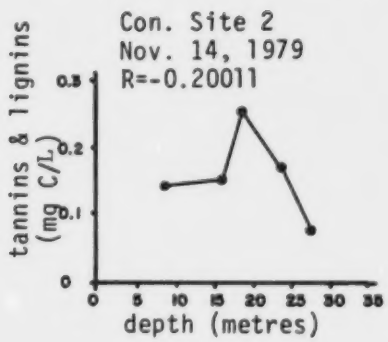
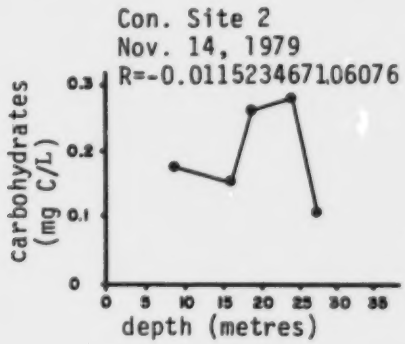
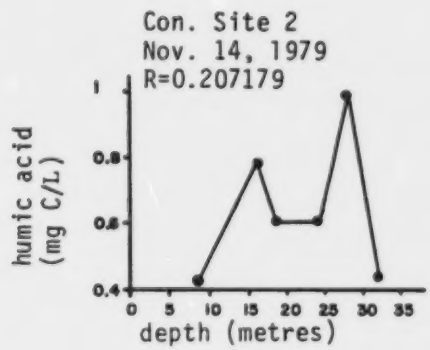
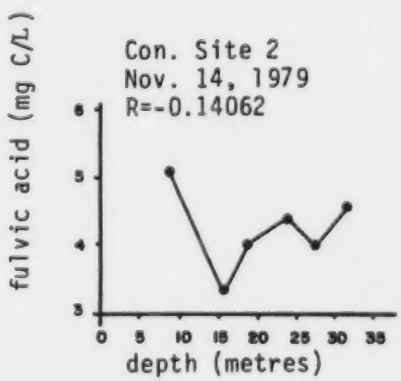


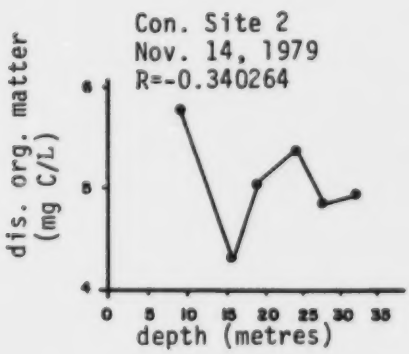
Figure 23. Relationship between organic parameters and depth inside and outside the Wabamun Mine - Nov. 14, 1979











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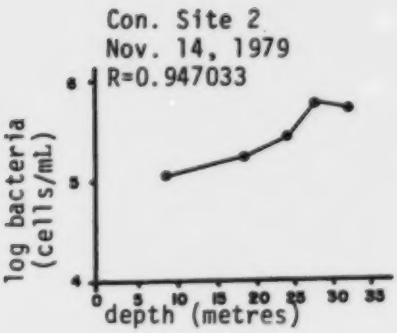

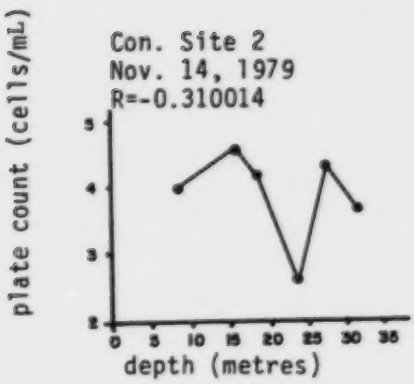

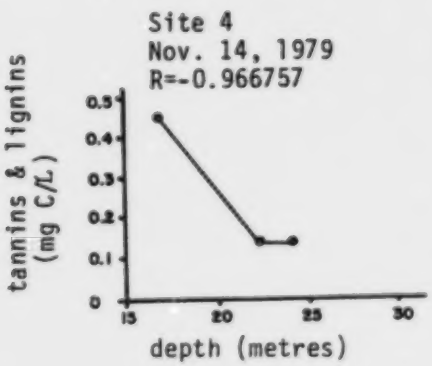

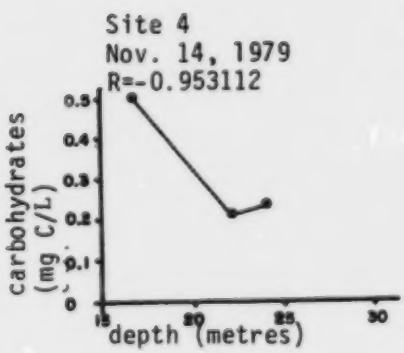

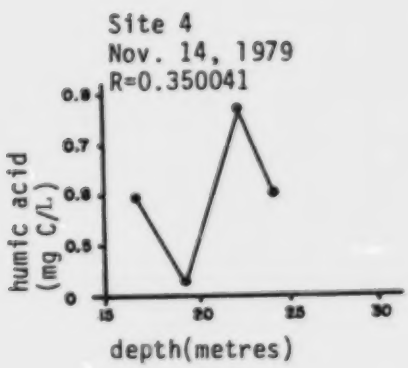

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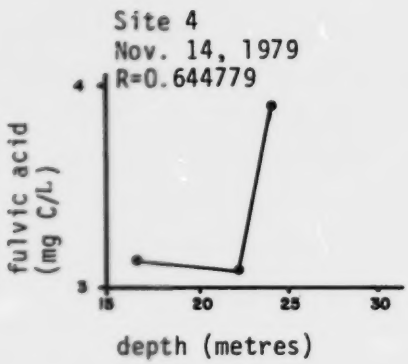
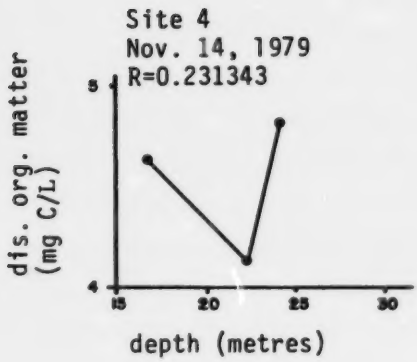
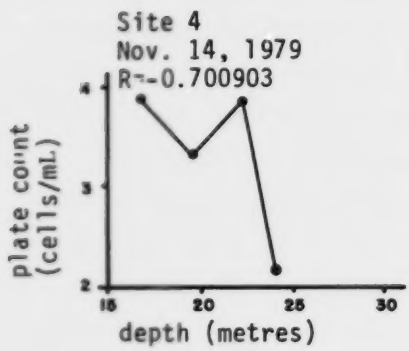
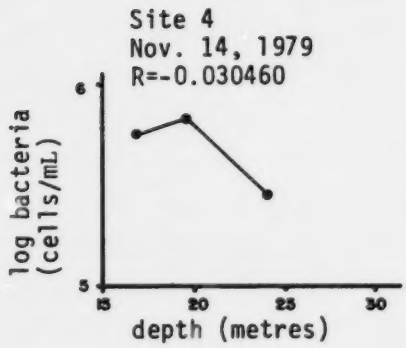








found with depth; rather, the magnitude of organic concentrations was evenly distributed. Some very definite reductions in concentration of tannins and lignins, carbohydrates, and dissolved organic matter with depth were found at Site 2 with r values over 0.9 in all three cases. The behaviour of humic and fulvic acids was more ambiguous. The range of concentrations of all organic compounds measured was comparable between all three sites.

Figure 20 reports the results found on March 22, 1979 at Control Site 2, Site 1, and Site 4. A more general decline in concentrations with depth was observed at Control Site 2 and the peak concentrations shifted to lower depths. This may have been influenced by the spring melt which was beginning at this time. Tannins and lignins were observed to increase slightly at Site 1 but the other results show no obvious trend. Concentration peaks were also found at Site 1 but at shallower depths. Definite decreases with depth were observed at Site 4 for all organic parameters except fulvic acids, but only two analyses were possible on that date. The range of concentrations was the same at all sites.

Figure 21 reports data collected on June 6, 1979 from Control Site 2, Site 1, and Site 7. The downward trend in concentration is still apparent at Control Site 2 and Site 7. Site 1 continues to show very little change with depth. The data collected on August 29, 1979 from Control Site 2, Site 1, and Site 7 are reported in Figure 22. Peak concentrations may still be observed at Control Site 2 between 17 and 27 m. At Site 1, carbohydrates and humic acids decreased with depth while tannins and lignins remained the same. Fulvic acids and dissolved organic matter both increased with depth. The same pattern was observed at Site 7 on this date. Figure 23 reports the data collected on November 14, 1979 at Site 4 and Control Site 2. Control Site 2 continues to show peaks in concentration but no trend with depth. At Site 4 tannins and lignins and carbohydrates decrease with depth. Dissolved organic matter did not change and fulvic acid showed a weak tendency to increase with depth.

A consideration of all the data in Figures 19 to 23 reveals an overall trend to decreasing concentration of organic parameters with depth at both control and mine installation nests when data are

examined for one sampling date at a time. Tannins and lignins almost invariably decline or remained the same, as did carbohydrates. Humic acid does not change very much but when it did, it went down in concentration. Fulvic acids did not show any trend, usually remaining the same. Dissolved organic matter either decreased or remained the same. Sporadic increases may be observed in the concentration of all parameters, particularly at Site 1, but usually the trend is downward. Groundwater appeared to be moving downward and laterally toward the south throughout the mine, although local interruptions caused by dewatering activities may have changed the lateral direction of flow (Anon. 1979). Deeper groundwaters are presumably older and the decreased concentration of organic compounds most probably reflects the effect of time upon degradation processes.

2.2.5 Changes in Organic Parameters Over Time Inside and Outside the Wabamun Mine

Concentrations of organic parameters have been plotted against time for all the installations at Control Site 2, Site 1, and Site 4 in Figures 24 to 26. Time is expressed as the day number from January 1, 1978 and all concentrations are in mg carbon/l. The trends of these plots are summarized in Table 22 which also includes a key relating the day number to the actual sampling date.

Although the concentration range changed over two orders of magnitude between parameters, it did not change very much between samples taken within any one site. Even changing the sampling site did not greatly affect the range of concentrations found for each parameter, inside or outside the mine. The changes which did occur were small but were fairly consistent. The plots in Figures 24 to 26 were carefully examined for seasonal patterns and comparisons may be made between control and mine site installations. An examination of these graphs and the summary table (Table 22) revealed that cyclic seasonal patterns are common, especially among the more refractory compounds (humic and fulvic acids). As these compounds make up the majority of dissolved organic matter, the trend is reflected within this measurement as well.

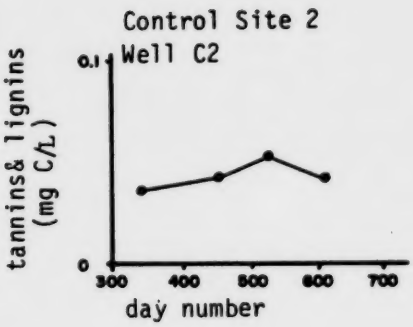
Table 22. Summary of changes in concentration of organic parameters over time at Control Site 2, Site 1, and Site 4 at Wabamun.

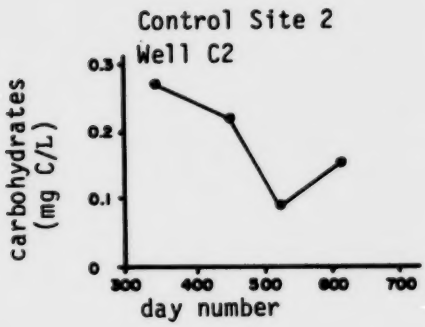
Installation	Tannins and Lignins	Carbohydrates	Humic Acid	Fulvic Acid	Dissolved Organic Carbon
WC2	same	down	cyclic	cyclic	cyclic
PC2A	cyclic	cyclic	cyclic	cyclic	cyclic
PC2B	cyclic	cyclic	cyclic	cyclic	cyclic
PC2C	up	cyclic	cyclic	cyclic	cyclic
PC2D	up	cyclic	cyclic	cyclic	cyclic
PC2E	up	cyclic	cyclic	cyclic	cyclic
W1	up	down	down	down	down
P1A	cyclic	up	down	cyclic	cyclic
P1B	cyclic	cyclic	cyclic	down	down
P1C	same	same	down	cyclic	cyclic
W4	up	up	cyclic	cyclic	cyclic
P4A	up	up	cyclic	cyclic	cyclic
P4C	cyclic	cyclic	cyclic	down	down

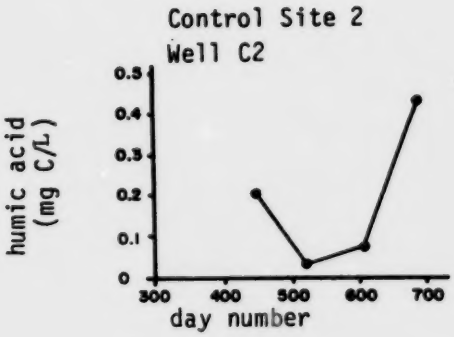
Sampling interval - December 5/78 to November 14/79

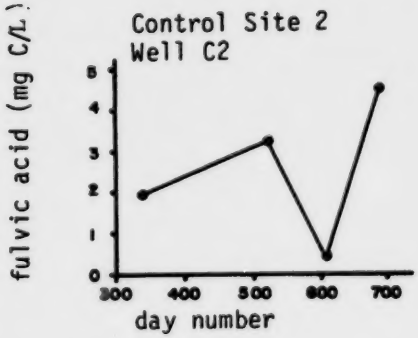
Day Number	Sampling Date
339	Dec. 5/78
446	Mar. 22/79
522	June 6/79
606	Aug. 29/79
683	Nov. 14/79

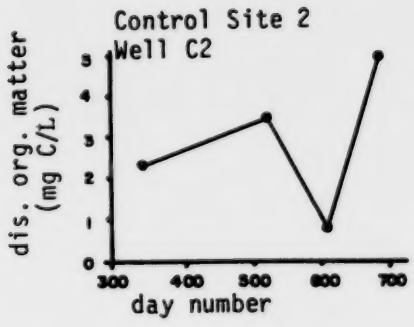
Figure 24. The concentration of organic parameters over time at Control Site 2.











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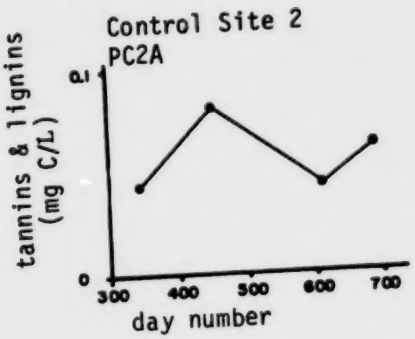

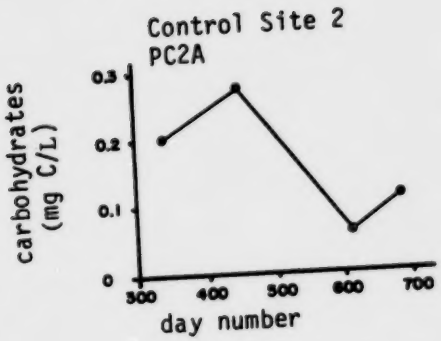

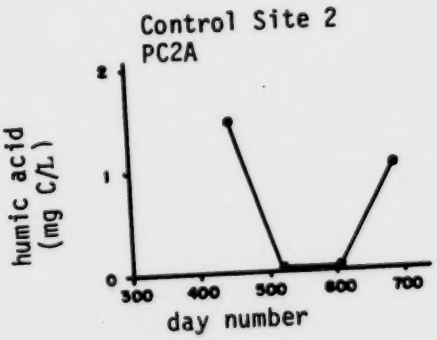

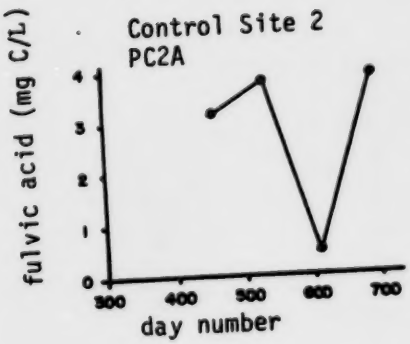

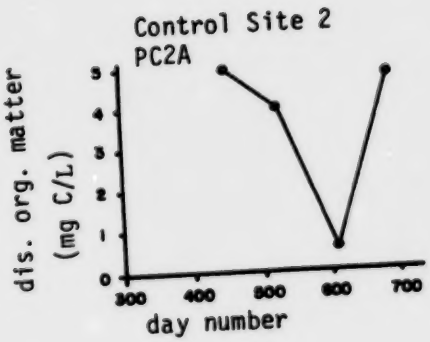

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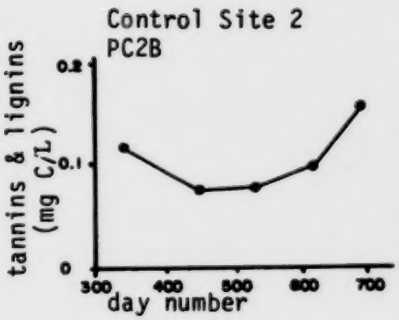

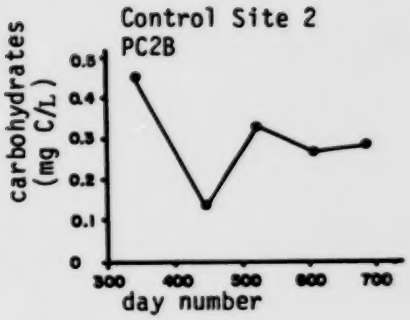

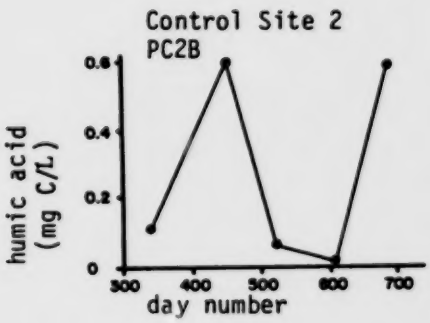

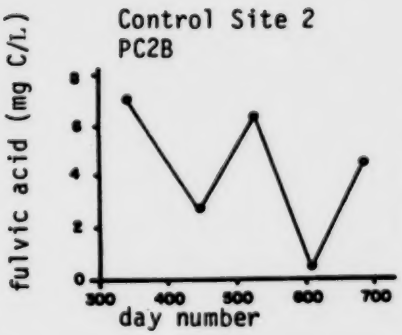

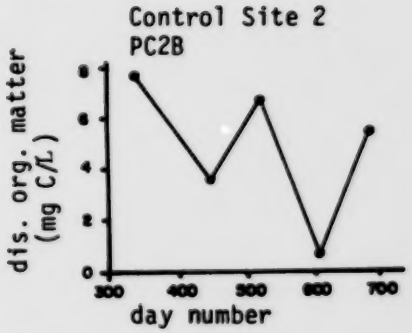

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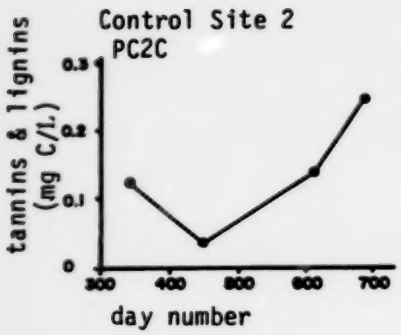

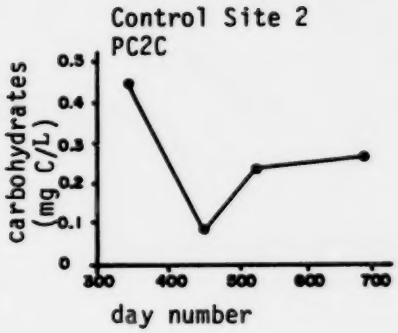

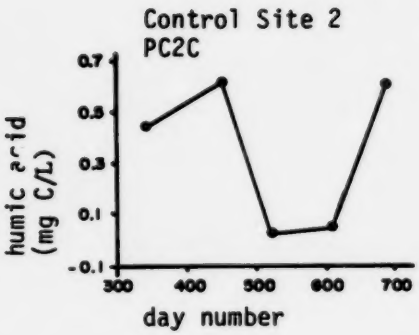

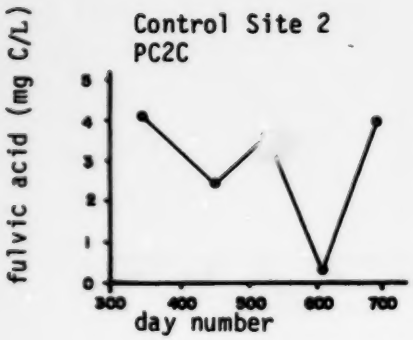

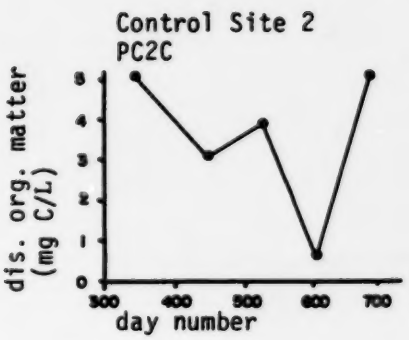

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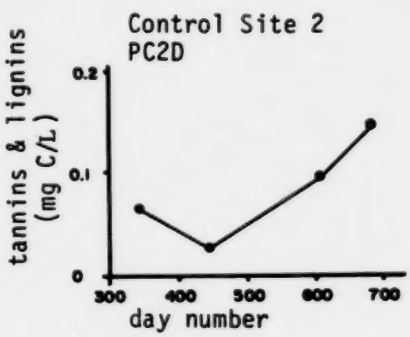

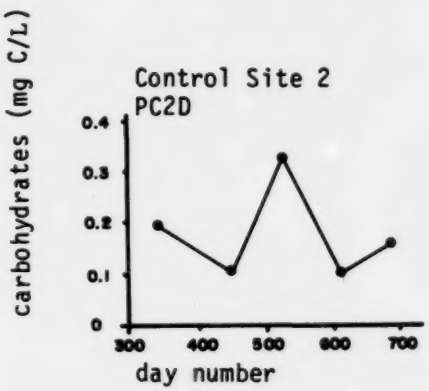

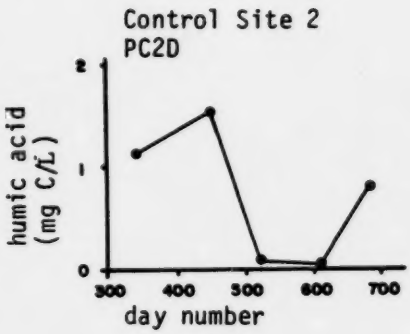

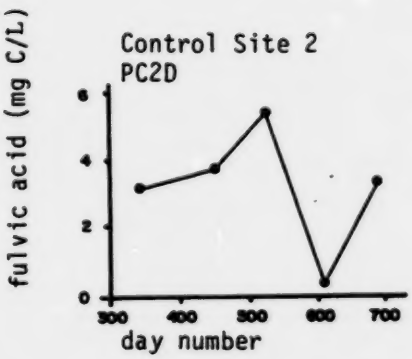

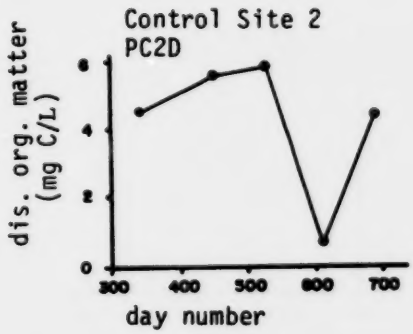

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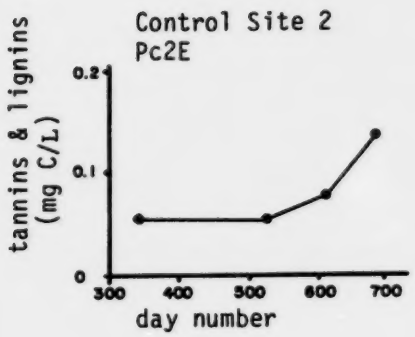
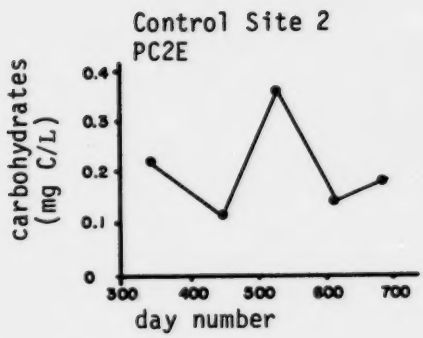
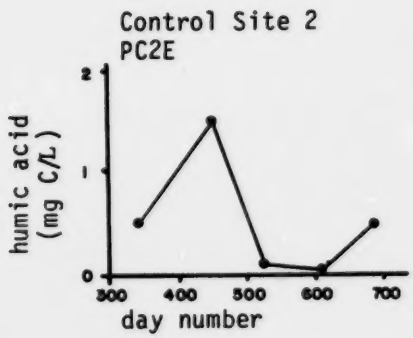
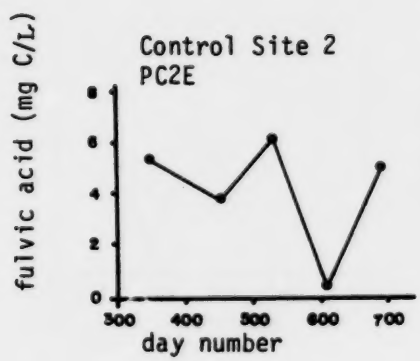








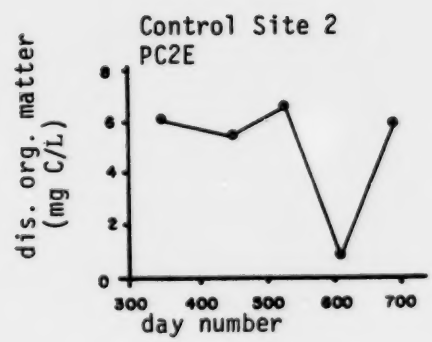
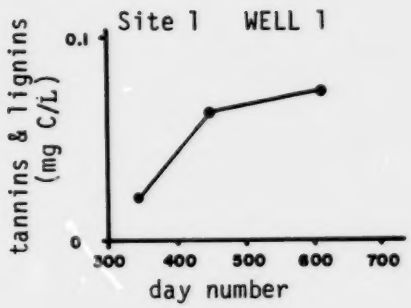
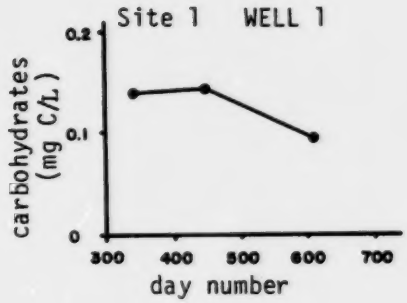
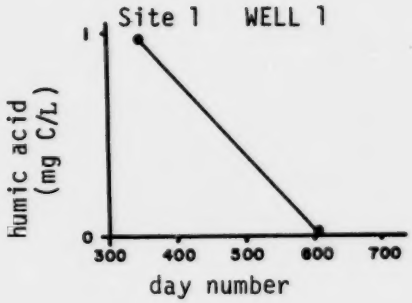
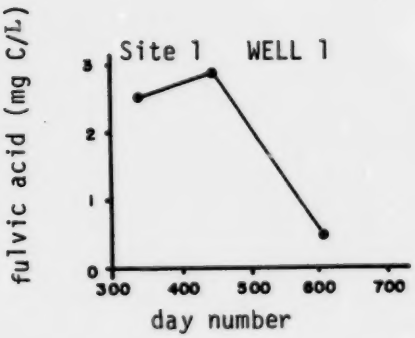


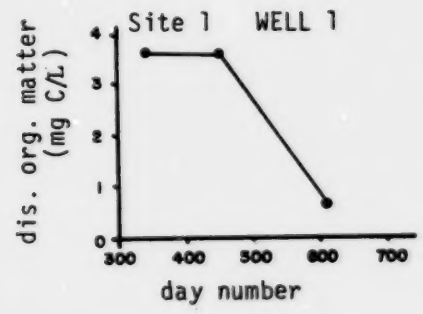
Figure 25. The concentration of organic parameters over time at Site 1.











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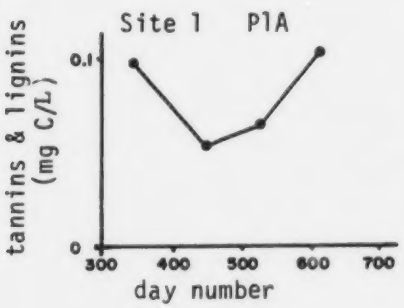

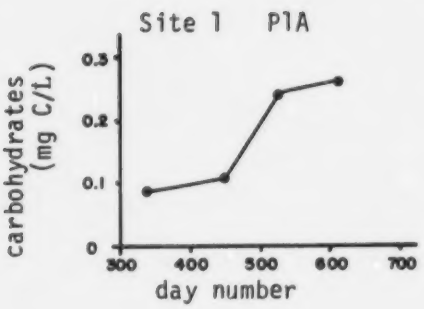

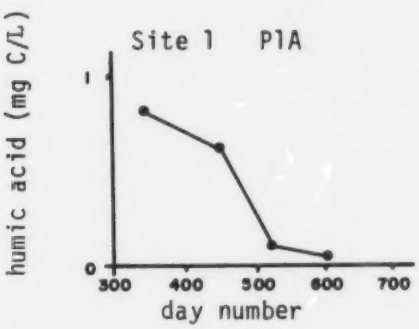

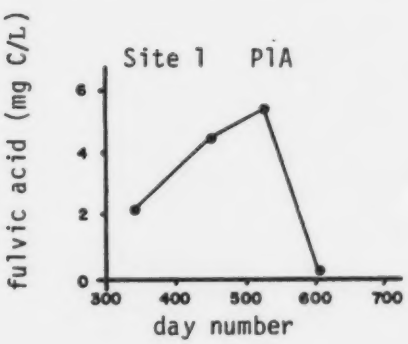

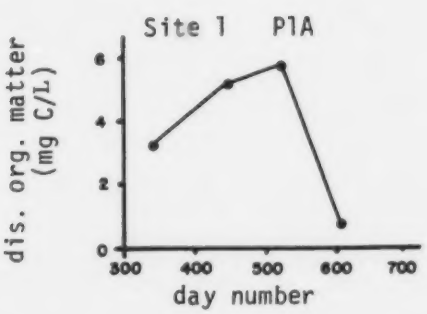

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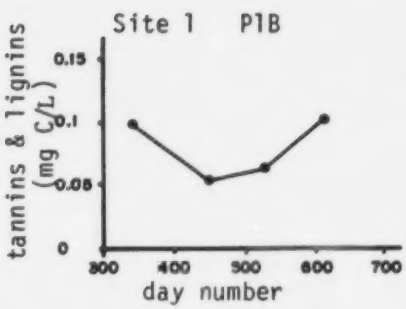

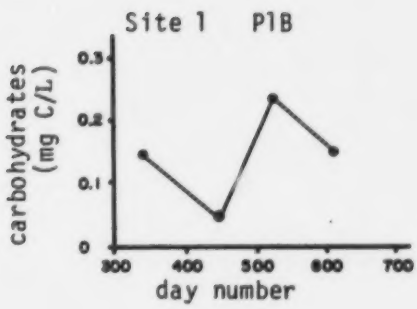

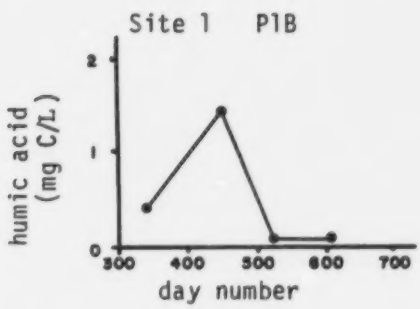

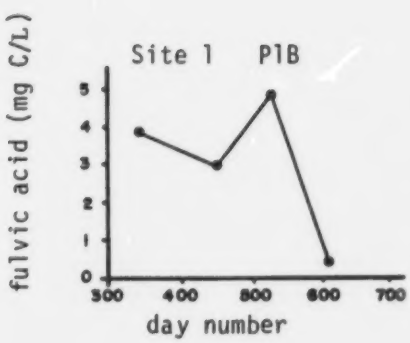

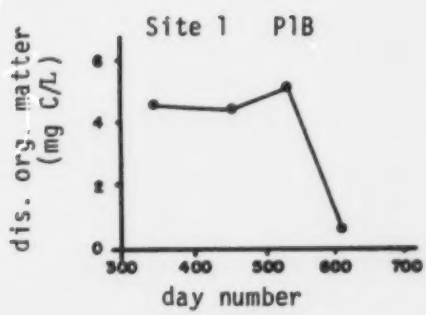

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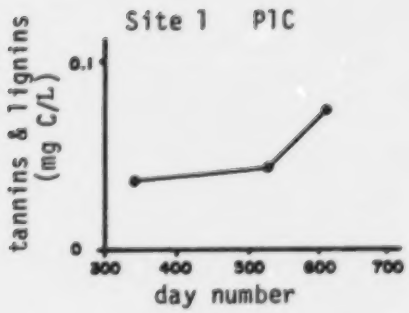
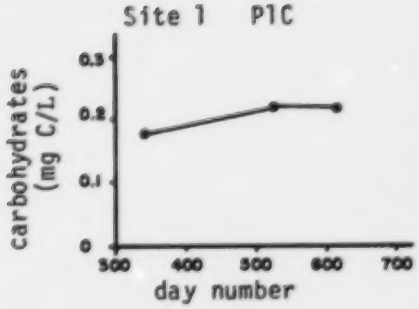
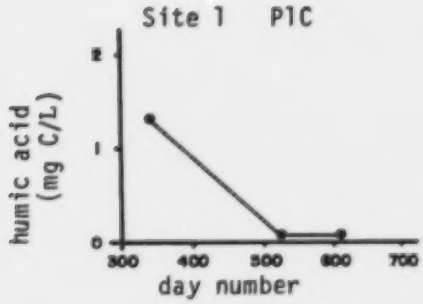
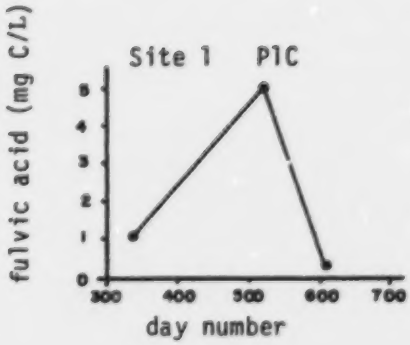








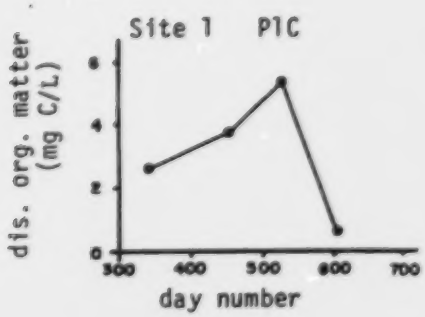
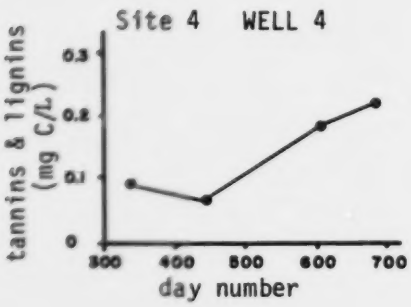
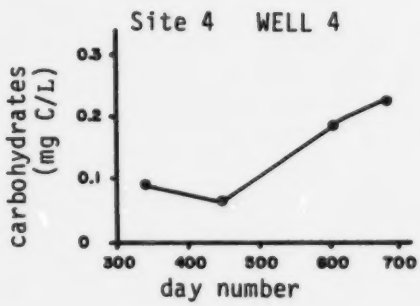
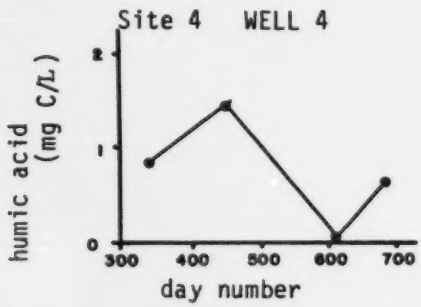
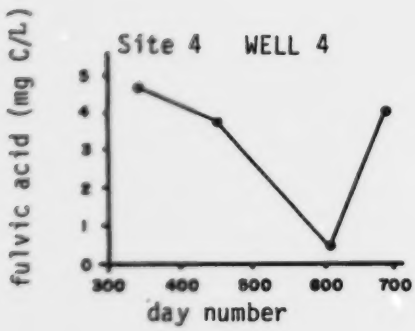


Figure 26. The concentration of organic parameters over time at Site 4.









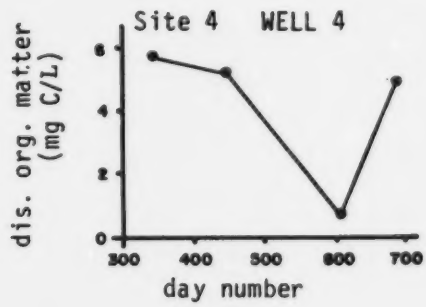
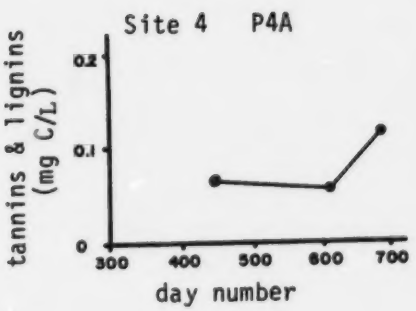
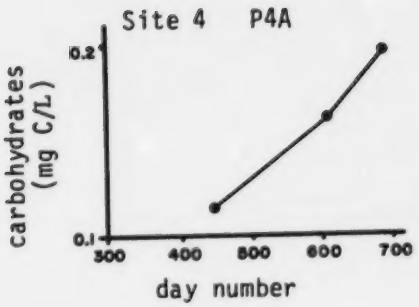
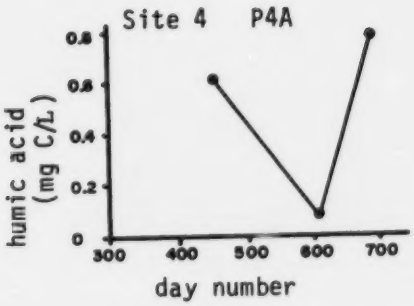
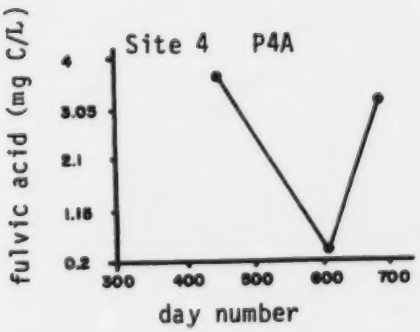


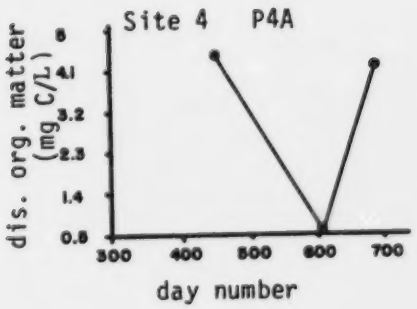
Figure 26. Continued.











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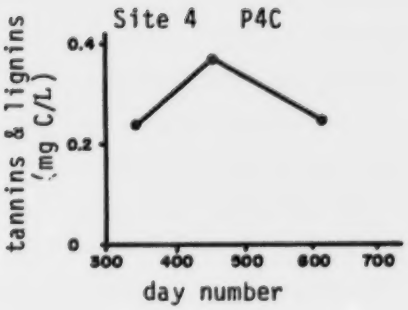
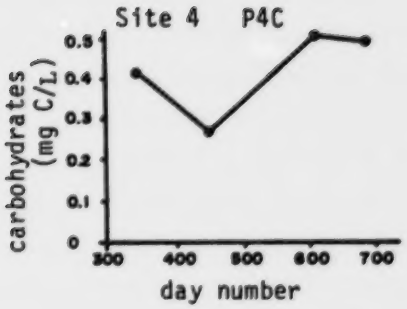
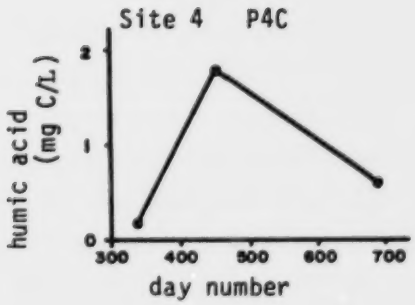
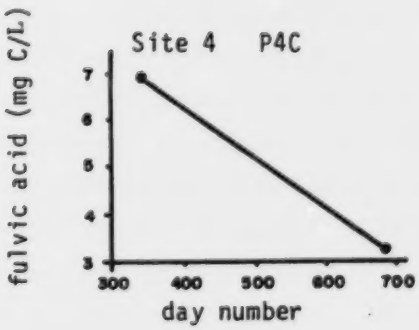
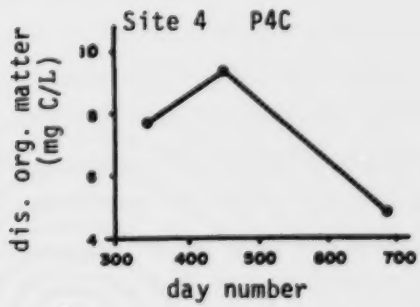










Cyclic patterns were more prevalent at the control site than at mine sites. Even carbohydrates and, occasionally, tannins and lignins showed seasonal patterns at Control Site 2, an observation much less common at Sites 1 or 4 within the mine. The lowest concentrations at all sites were invariably found in the spring or early summer, suggesting a correlation with the spring melt. The spring and early summer are periods of intense biological activity, particularly in shallow soil horizons. Degradation of organic material in the unsaturated soil zone may be occurring more rapidly at this time of year than in other seasons. As these soil zones contribute large amounts of organic material to infiltrating water on its way to the saturated zone (Wallis et al. in press), the total loading from surface sources may be reduced in the spring and early summer. This process, in combination with the larger volumes of infiltrating melt waters in the spring, could explain the reduction in concentrations observed. The highest seasonal concentrations were usually found in the fall or winter but sometimes in the early spring as well. No obvious differences may be observed between the mine and control sites with respect to the timing or magnitude of high concentrations. Higher concentration of organic matter in groundwaters is undoubtably related to the degradation of shallow soil organic material in recharge areas such as these. Variations in infiltration capacity and precipitation may cause differences in the timing of seasonal concentration peaks, although the most profound changes clearly occur in the spring.

These data suggest that downward water movements are fairly rapid in the spring and early summer although hydraulic head measurements made by Alberta Environment (Anon. 1979) do not strongly support this. If the decreases in concentrations observed in the spring and early summer are not related to the infiltration of spring melt water, it is not apparent why this should only occur in the spring. It is more probable that degradation of organic material in groundwater occurs slowly at a fairly constant rate after an initial burst of activity in the spring. Degradation occurs most slowly in the winter under cold, dry conditions, so concentrations build up again in the fall and winter. This hypothesis is put forward as a tentative explanation of the cyclic patterns observed in the concentration of organic material in groundwater.

2.2.6 Changes in the Concentration of Organic Parameters over a Cross-Section of Wells and Piezometers at Wabamun

Groundwater flows through the Whitewood Mine from the north to Lake Wabamun (Anon. 1979). This permits the selection of data from wells and piezometers along a transect from upstream to downstream in order to identify any changes in the concentration of organic parameters as groundwater flows through the mine. In order to do this, the measurements taken at Control Site 2 were assumed to be representative of the organic content of groundwater before it reaches the disturbed portion of the mine. The transect used is identified as the line F to F' in Figure 1 and the data are plotted in Figures 27 and 28. Figure 27 is made up of data from Well C2 (identified as installation 1 on the x-axis), Well 2 (2), Well 4 (3), Well 7 (4), and Well 6 (5). Wells were installed into the coal seams which remain in the Scollard Member below the base of the spoil material inside the mine. Well C2 was completed in the uppermost coal seam. In Figure 28, data are plotted from the deepest piezometer at the same sites used in Figure 27. The installations used are PC2A (identified as Installation 10 on the x-axis), P2A (11), P4A (12), P7A (13), and P6C (14). All of these are completed in the spoil material just above the old floor of the mine.

A comparison of the data in Figures 27 and 28 reveals that different processes are taking place between the wells and piezometers (coal and spoil material). In addition, the concentrations of the five organic parameters measured do not vary in unison although clear trends may be seen. In a few cases the data do not show any trend at all but, generally, the concentration along the transect goes up or down in a clear pattern. All of the organic parameters measured increased in concentration occasionally but the reverse was usually the rule. Sometimes the concentration in the control well or piezometer is much lower than that found in the upstream portions of the mine causing the curve to rise sharply between Control Site 2 and Well 2, after which it usually decreased to the control site concentration. The reverse was found to be true on only two occasions. In the wells, concentrations tended to decrease in December, June, and August and to increase in March. In

Figure 27. Concentration of organic parameters measured in wells along the cross-section line F to F' at Wabamun.

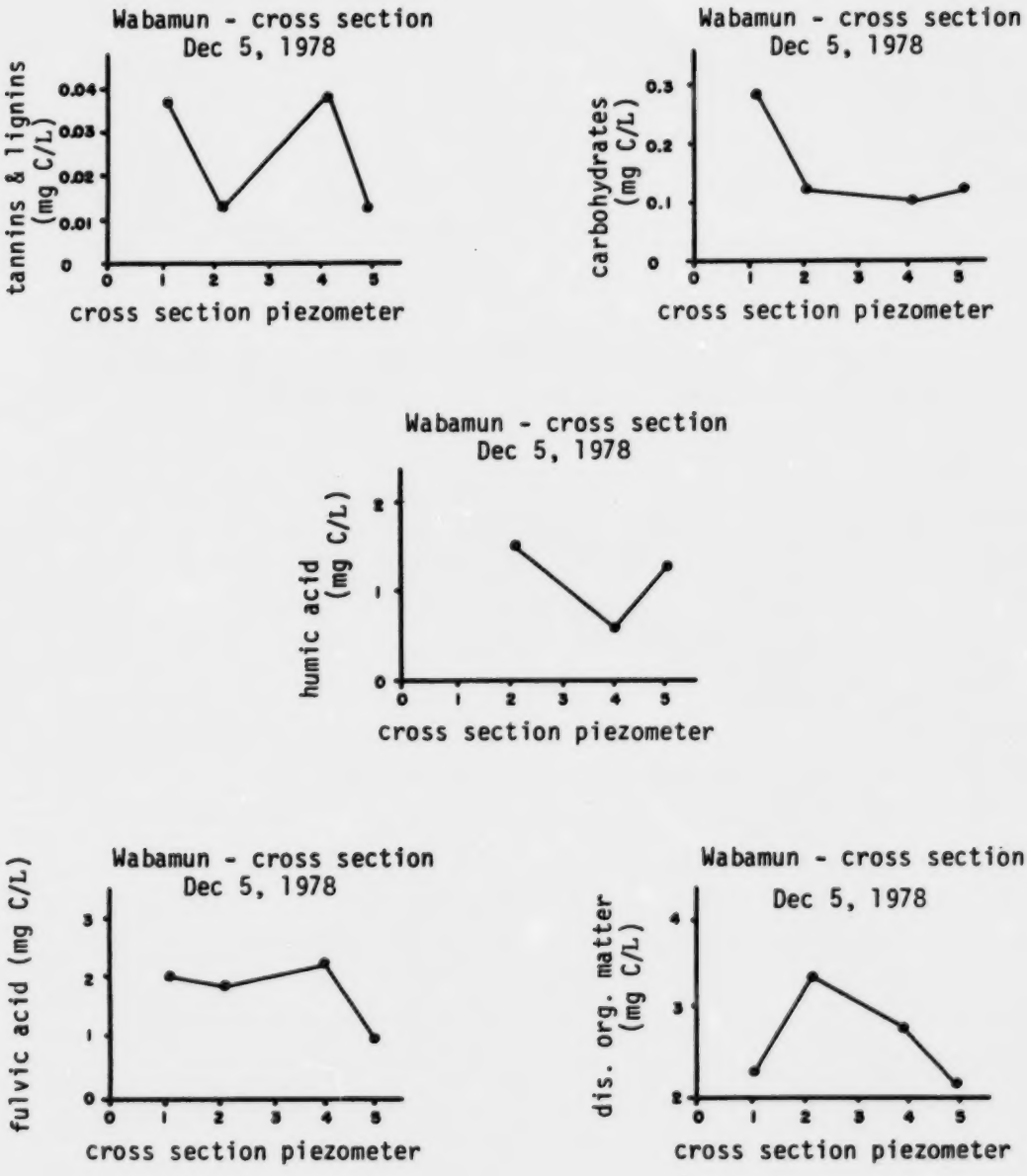
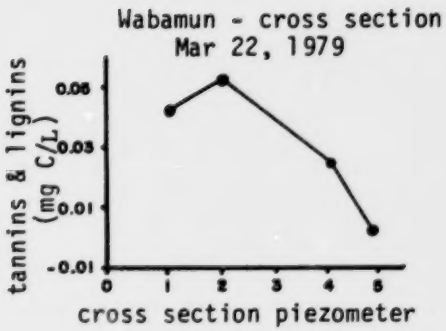
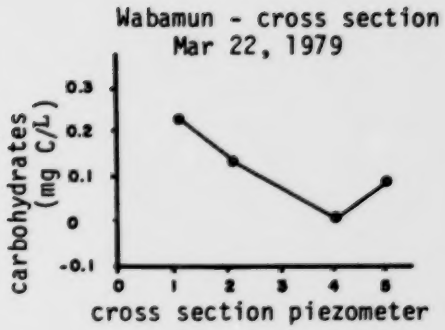
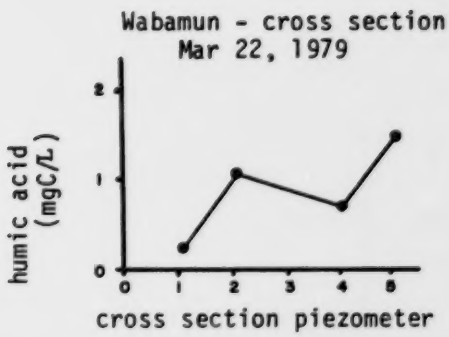
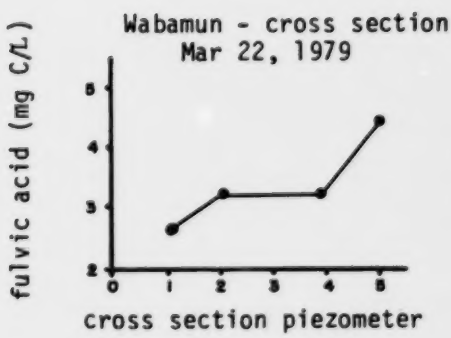


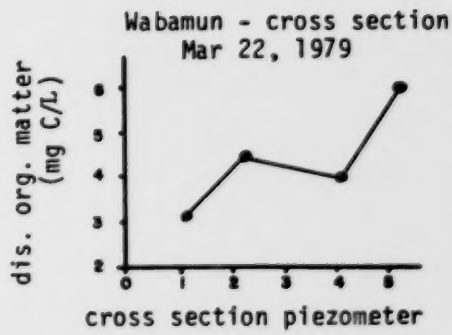
Figure 27. Continued.











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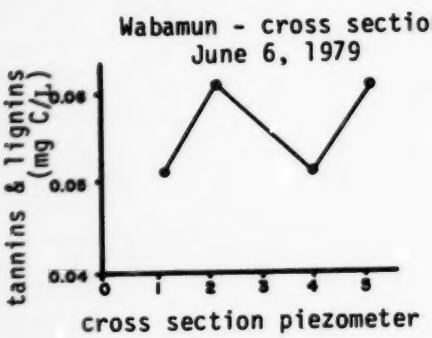

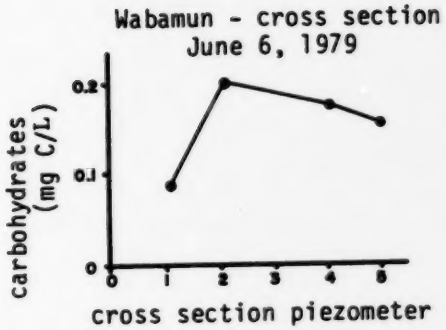

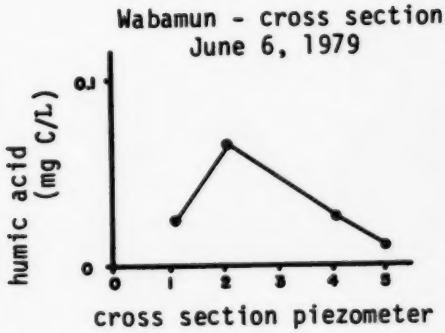

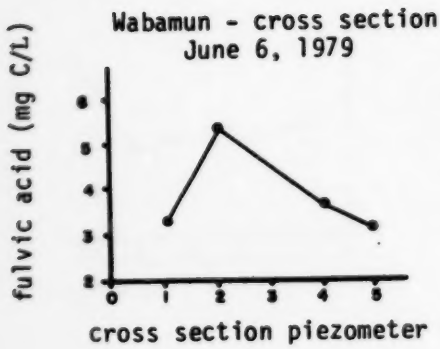

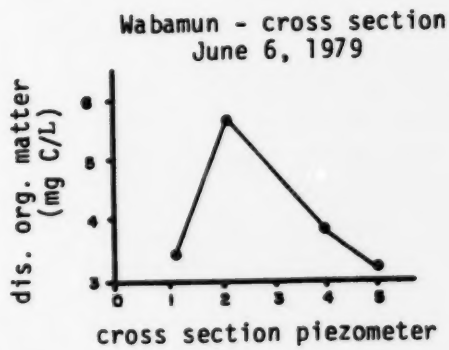

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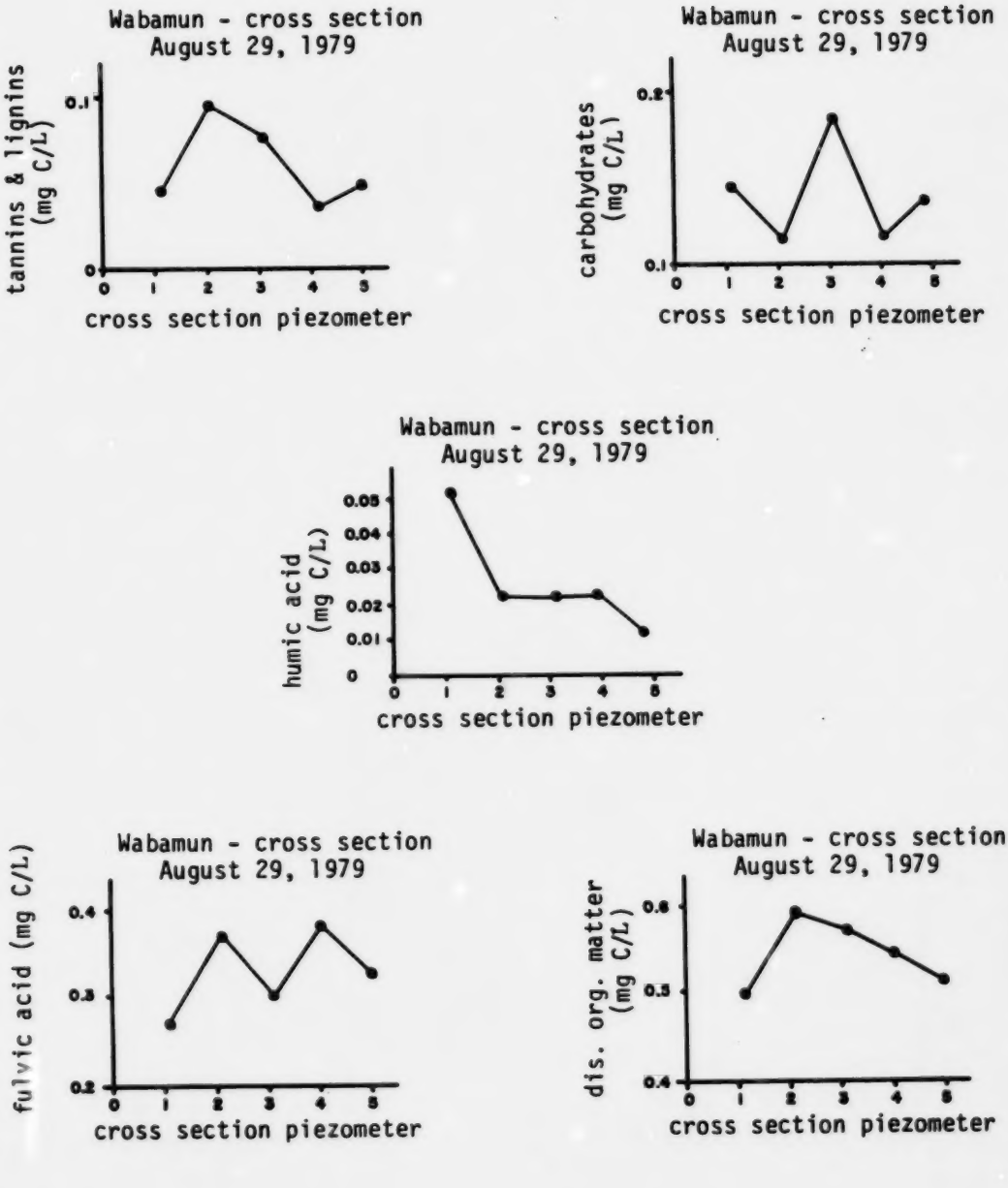
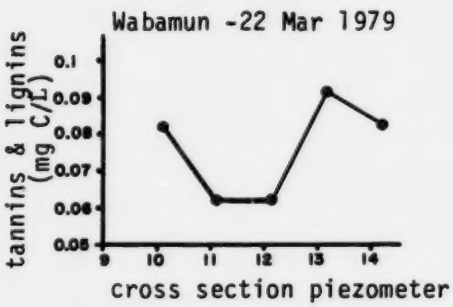
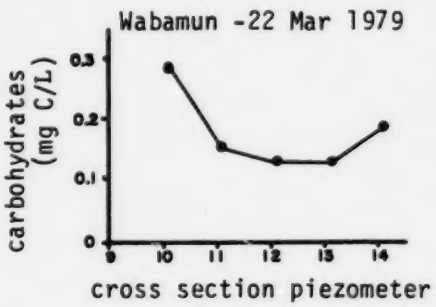
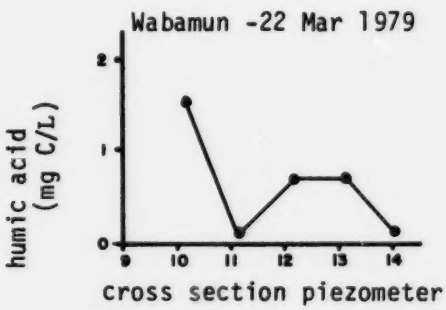
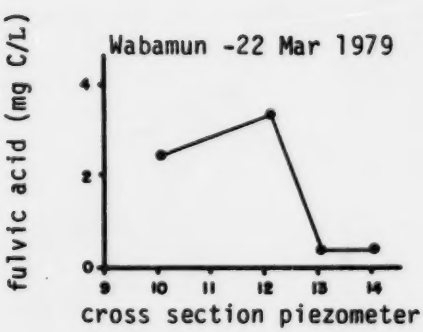


Figure 28. Concentration of organic parameters measured in mine spoil by the deepest piezometer in each site along the cross-section line F to F' at Wabamun.









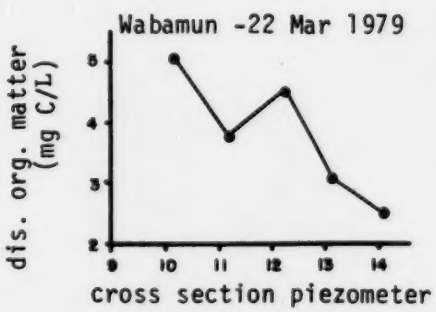
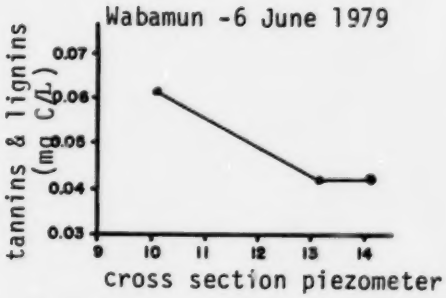
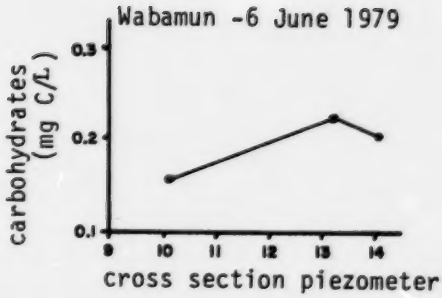
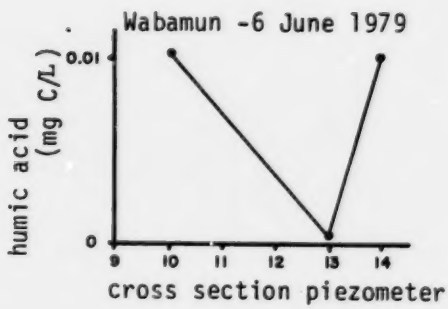
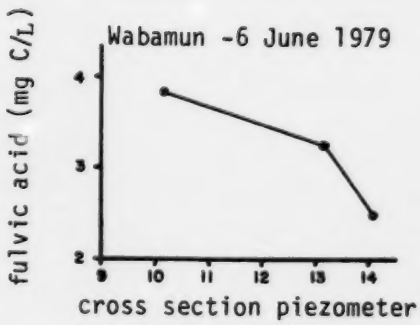


Figure 28. Continued.









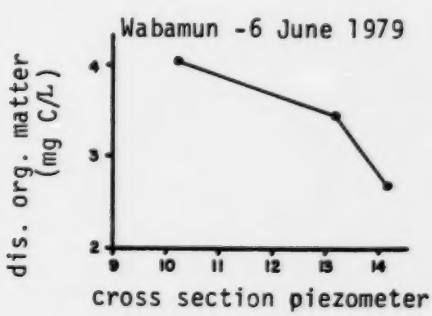
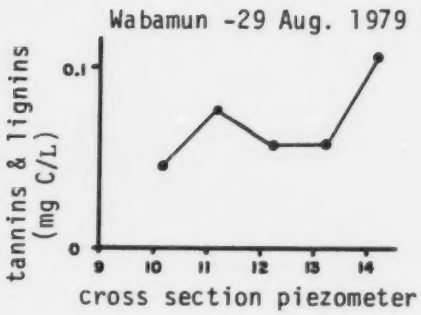
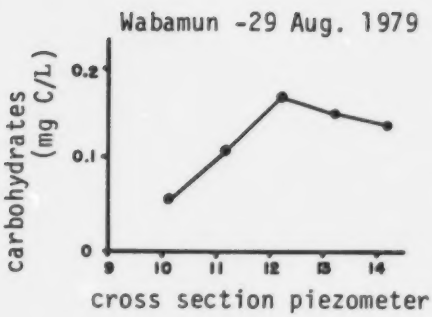
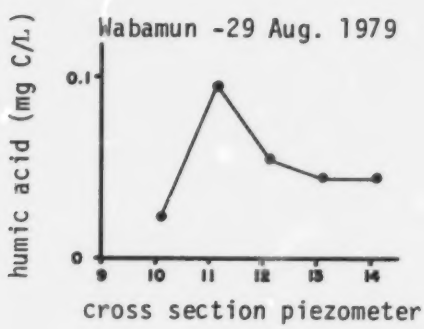
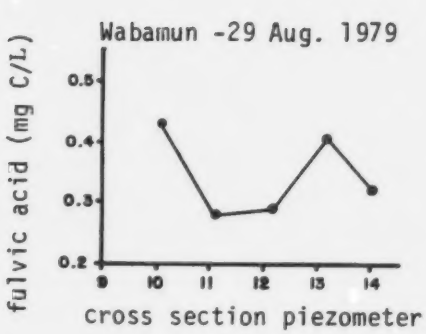


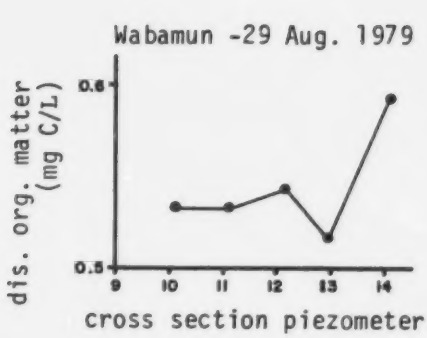
Figure 28. Concluded.











the piezometers the level of organic compounds tends to decrease in March and June and go up in August as water passed through the mine. In general, it may be said that the concentrations of organic compounds in the groundwaters passing through the mine usually decrease in the spring for the piezometers and in the summer for the wells. These data suggest that groundwater communication between spoil and bedrock is not very intimate. Nevertheless, it is important that concentrations of organic compounds generally decreased as groundwater passed through the mine in both the spoil aquifers and the remaining coal seams in the bedrock underneath.

2.2.7 Amino Acids at Wabamun

On June 6 (1979), a number of samples were taken for amino acid analysis in conjunction with regular sampling. From the results reported in Figure 29, it may be seen that amino acids are present in both the free and combined form at concentrations ranging between 5 and 100 g/L. The key to the amino acids on the x-axis may be found in Table 20.

The concentrations of amino acids found were very similar to those found at Canmore (see Section 2.2.1.7) and those amino acids found between numbers 15 and 18 (aspartic acid, glutamic acid, lysine, tyrosine) were the most abundant. Of these, glutamic acid was the most common. Based on the data in Figure 29, some of the other amino acids at the other end of the x-axis (particularly alanine, valine, and glycine) were more common in spoil material than in the coal seams, especially in the combined form. As found at Canmore, the combined amino acids far outnumbered the free amino acids at all sites sampled, presumably because of the greater energy input required to degrade them either chemically or biologically. In Figure 29, there is a small tendency towards a decrease of combined amino acids with depth in the spoil material and in the bedrock. This appears to be true at Site 6 and partially at Site 7 (except for P7A). This condition also holds true at Control Site 2.

In general, amino acids were present at Wabamun in the same range of concentrations as at Canmore, mostly in the combined form. There was a tendency towards a decrease in concentration with depth and glutamic acid was the most stable amino acid. Somewhat larger

Figure 29. Amino acid data from Wabamun from samples taken on 6 June, 1979. The key to amino acids on the x-axis may be found in Table 20.

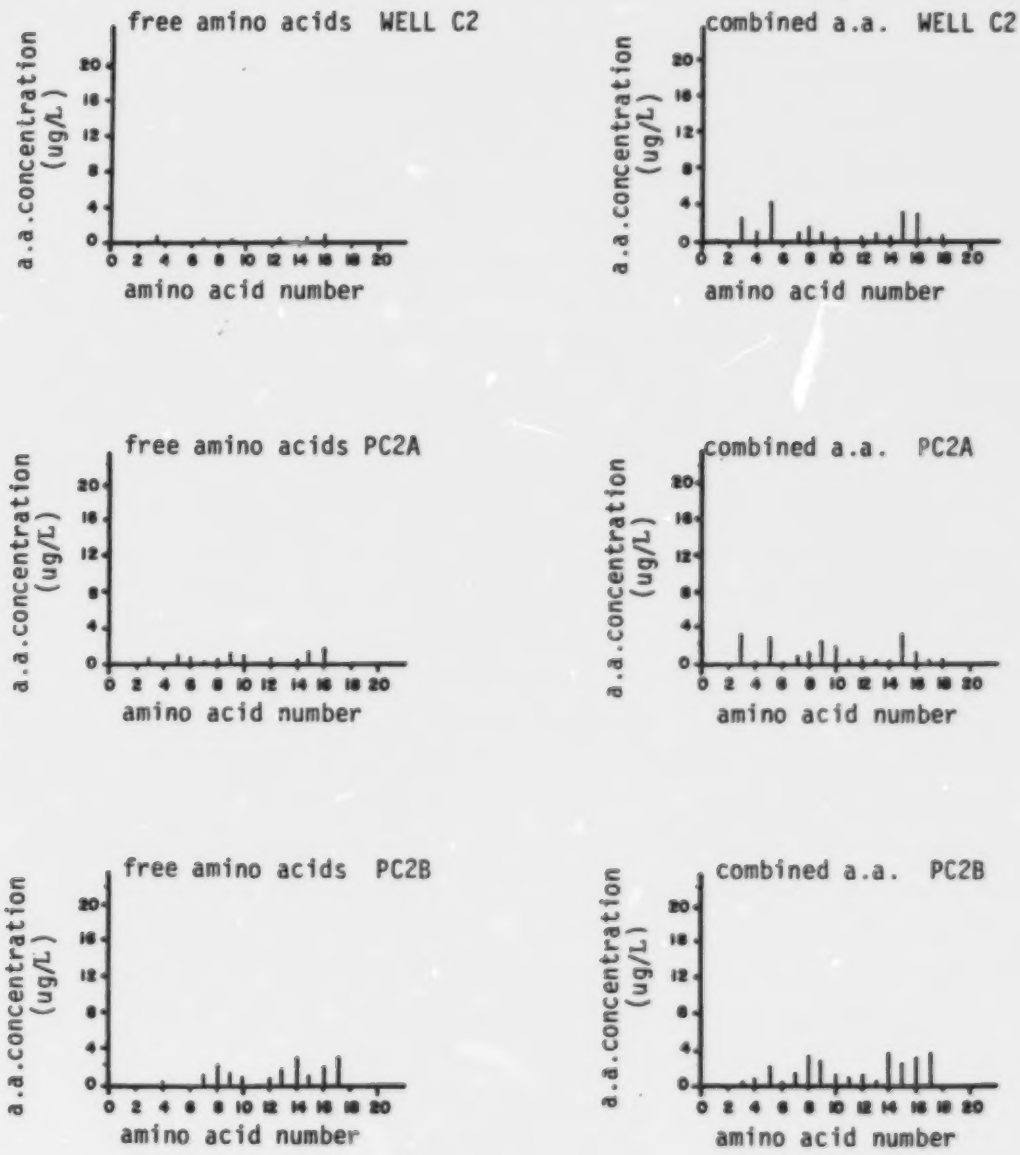
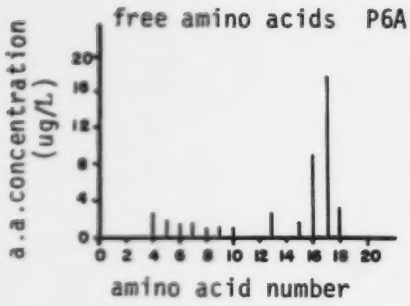
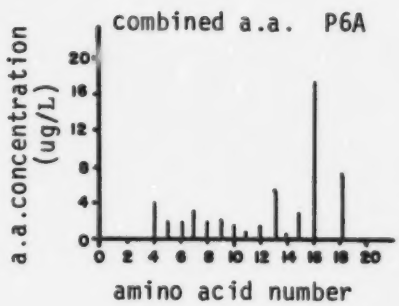
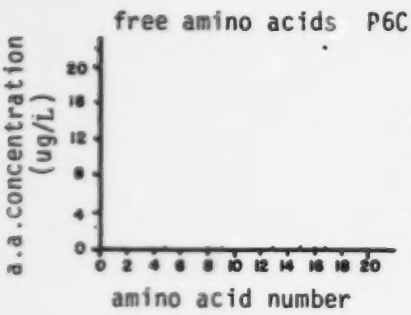
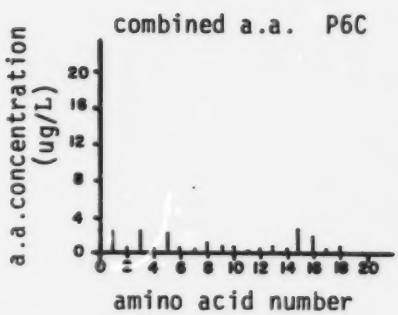

free amino acids WELL C2
combined a.a. WELL C2
free amino acids PC2A
combined a.a. PC2A
free amino acids PC2B
combined a.a. PC2B
a.a.concentration (ug/L)
amino acid number
0 2 4 6 8 10 12 14 16 18 20
0 4 8 12 16 20

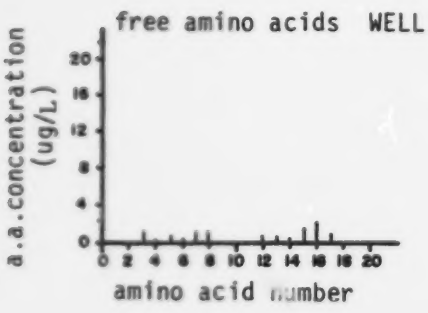
Figure 29. Continued.











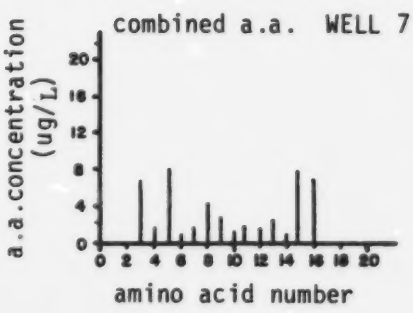


Figure 29. Continued.

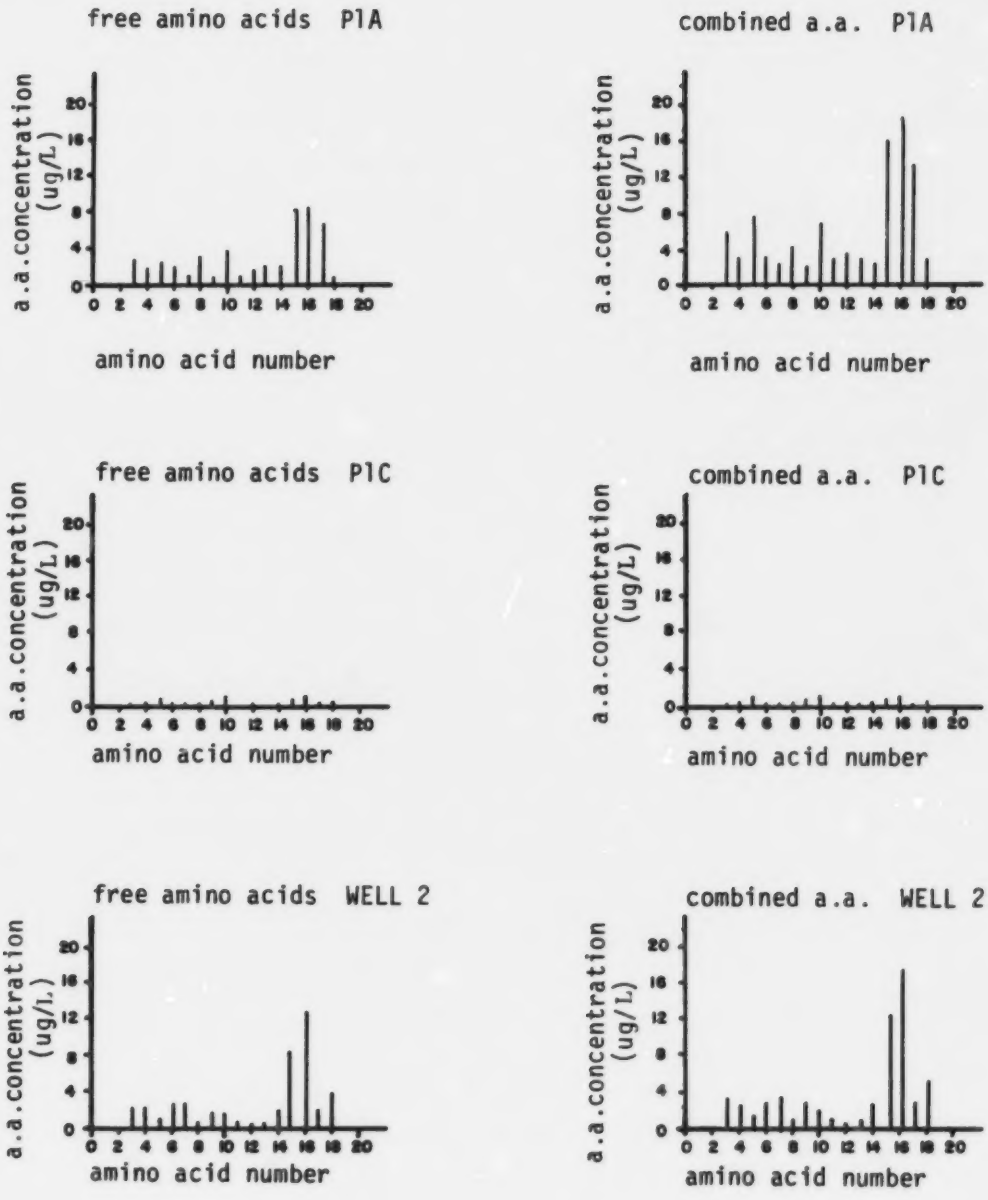
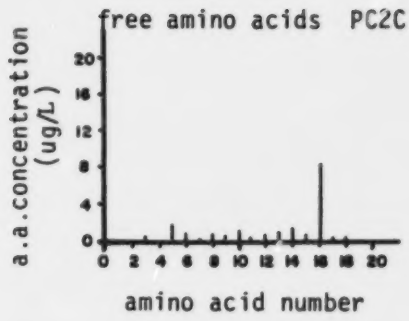
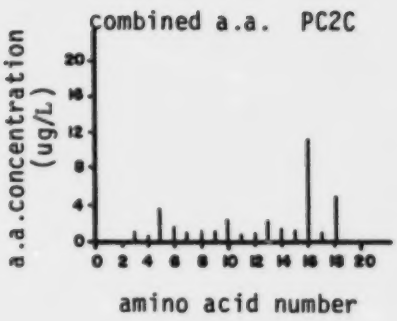
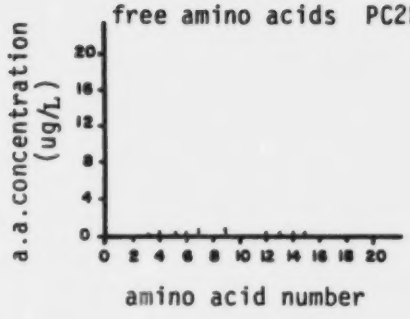
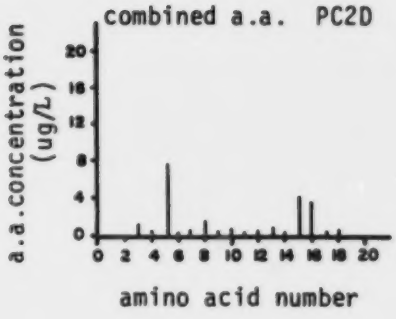

free amino acids P1A
combined a.a. P1A
free amino acids P1C
combined a.a. P1C
free amino acids WELL 2
combined a.a. WELL 2
a.a.concentration (ug/L)
amino acid number
0 2 4 6 8 10 12 14 16 18 20
0 4 8 12 16 20

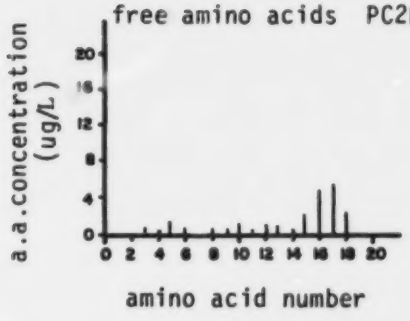
Figure 29. Continued.











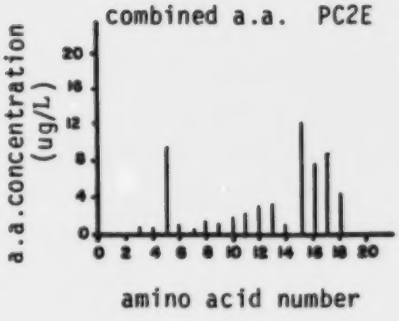
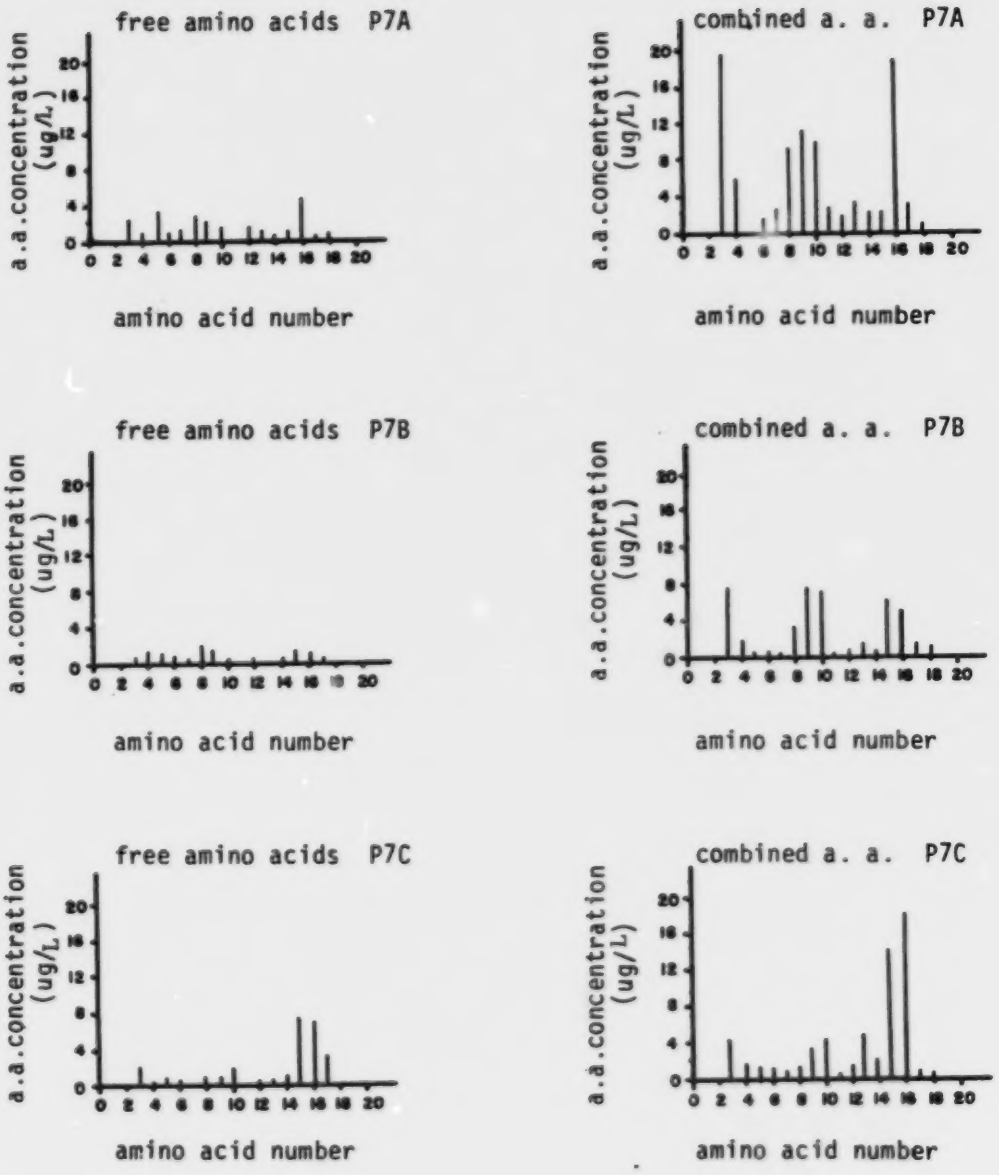


Figure 29. Concluded.



amounts of combined alanine, valine, and glycine were observed in spoil material compared with coal in the bedrock.

2.3 THE INFLUENCE OF REVERT UPON ORGANIC AND INORGANIC GROUNDWATER CHEMISTRY

The organic drilling mud Revert was used extensively in the installation of wells and piezometers at Wabamun. Revert is a plant-derived polymer consisting largely of galactomannin (82%) and smaller amounts of protein (5%) and crude fiber (2%). It is made from the South American Guar bean and is an edible carbohydrate. For this reason it affords an excellent substrate for bacterial growth which must be inhibited by formaldehyde when the mud is used for a long period of time in warm weather. The principal advantage of using Revert is that it does break down naturally by microbial action and it can be 'broken' almost instantly by the addition of agents such as Fastbreak, calcium hypochlorite, or certain enzymes. Revert contains the natural bacteria which are always associated with plant material, but no additional micro-organisms are added. The Johnson Company, which makes this product, recommends that such agents be added upon the completion of drilling so that the viscosity of the mud is rapidly decreased and the Revert remaining in the hole can be pumped out during normal well development. Well logs indicate that Revert was used to drill the 10 cm wells at each site but no logs are available for the 5 cm piezometers. No mention is made of the use of any breaking agents. Information obtained from Mr. Allen Kerr, Head of Groundwater Branch, revealed that Revert was also used whenever it was necessary to penetrate rock which would include at least the deepest piezometer at each site . As the same rig was used to install the piezometers as the wells, it is assumed that Revert was used at all nest sites and that all wells and piezometers which are not designated as augered holes are affected. This does not include the extra piezometers augered in by the Groundwater Branch in the summer of 1978 for comparison purposes. These piezometers were installed at Control Site 2, near Site 1, and along the northern portion of the mine ring road (see Figure 1 - augered piezometers A16 to 22). Unfortunately, not all

of these piezometers delivered water consistently but enough data were collected (see Table 23) to show that there were no obvious differences in organic chemistry between those holes which were exposed to Revert and those which were not. If changes occurred because of the use of Revert, the effects had disappeared before the inception of this study.

Although a comparison of the organic chemistry of installations which were probably contaminated by Revert and those which were not failed to reveal any important changes (Table 23), data collected by Groundwater Branch before this study began show that high levels of organic matter, present in many wells and piezometers after they were installed, subsequently declined (Anon. 1979). This made the evaluation of the possible effects of using Revert on organic and inorganic chemistry very hard to define. Because of this, some indirect techniques were employed.

Because Revert is primarily composed of carbohydrate, it is very susceptible to microbial attack. Organic matter can be mineralized to carbon dioxide which will dissolve in the groundwater to become bicarbonate ion at the basic pH common to Wabamun groundwater and aiding in the dissolution of carbonate minerals. This situation makes the use of the stable isotope of carbon, ^{13}C, possible to determine whether or not this process took place after the wells were drilled with Revert. It is well known (Wallis et al. in press) that micro-organisms will preferentially select the lighter ^{12}C isotope of carbon over the less common (about 1% of the ^{12}C content - Degens 1969) ^{13}C isotope. This means that the remaining organic matter in solution will become progressively 'heavier' with respect to ^{13}C and that the CO_2 given off by respiration will be very 'light' with respect to ^{13}C. As this CO_2 becomes bicarbonate ion, the pool of dissolved inorganic carbon will become lighter. Unfortunately the ^{13}C content of Revert and coal is the same, about -25 parts per mille (with respect to the PDB standard - Degens 1969) because they are both derived from plant material with similar photosynthetic cycles. Revert is a much better food substrate than coal, however, so it is assumed that any shift that occurred in the ^{13}C content of organic carbon in groundwater was caused by mineralization of the former. This was checked by

Table 23. Comparison of average chemistry (in mg C/L) of groundwater sampled from wells and piezometers affected by Revert and those augered installations which were not.

	Revert	No Revert
Tannins and Lignins	0.09 ± 0.08	0.11 ± 0.10
Carbohydrates	0.29 ± 0.39	0.23 ± 0.15
Humic Acid	0.61 ± 0.54	0.47 ± 0.50
Fulvic Acid	3.40 ± 2.22	2.74 ± 2.16
Dissolved Organic Matter	4.41 ± 2.39	3.55 ± 2.33

Mean ± Standard Deviation

Units - mg carbon/L

comparing the data from augered holes (free of Revert) and rotary drilled holes.

The ^{13}C content of inorganic carbon of marine carbonates is 0 parts per mille with respect to the PDB standard (Degens 1969). Chemical fractionation and biological influences usually result in a concentration of between -5 and -11 parts per mille in bicarbonate ions (Hoefs 1973). If large amounts of 'light' CO_2 are added to groundwater from the oxidation of a rich source of organic matter, a shift to lighter concentrations of ^{13}C (more negative values) in the dissolved bicarbonate may be expected. At the same time, the ^{13}C content of the remaining organic matter should increase (become less negative) with respect to the PDB standard. If such a shift has occurred, it may be interpreted as evidence for the oxidation of a large amount of organic matter, presumably Revert.

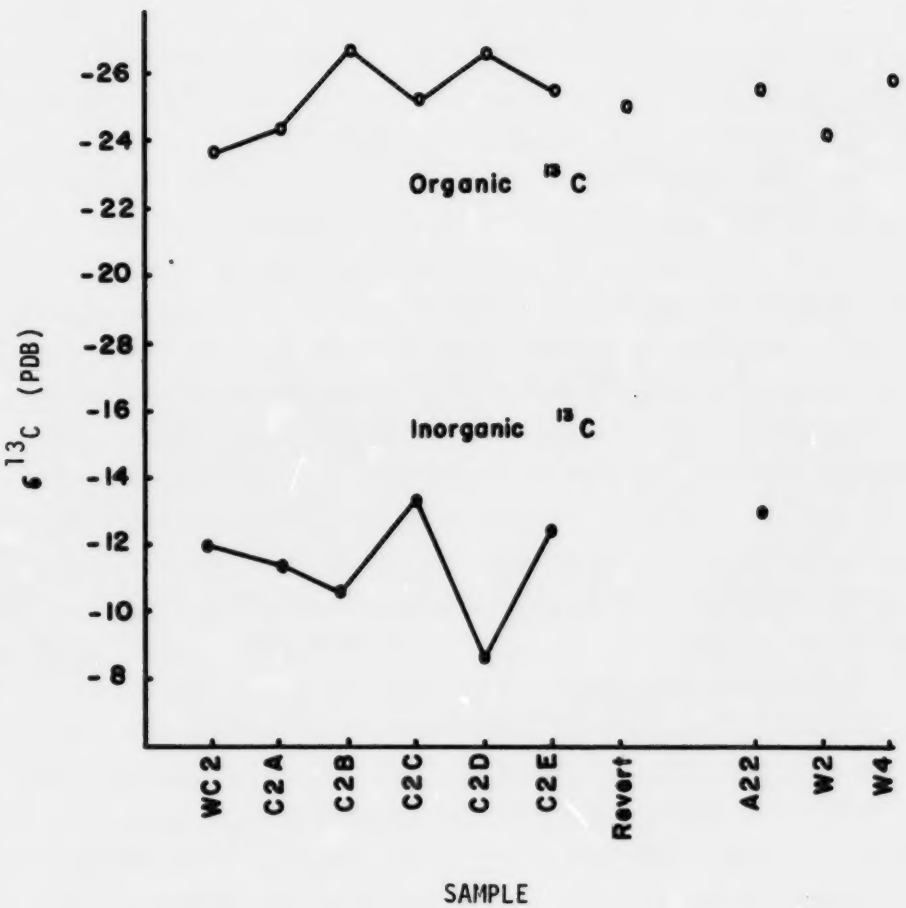
In order to check this, several samples were taken from Control Site 2, Well 2, Well 4, and from A22 (uncontaminated by Revert). Unfortunately, A22 was the only augered piezometer which yielded enough water (10 L) for ^{13}C analysis at the Control Site and was the only control possible. Control Site 2 was chosen in order to minimize any possible effects of coal mixed into the spoil overburden. Samples were prepared for mass spectrometric analysis using a wet oxidation device described in Wallis et al. (1979). Briefly, this consists of a large vessel seated in a heating mantle with a condenser mounted in the neck. Oxygen (cleansed of CO_2 by Ascarite) is bubbled into the vessel and flows through the solution, up into the condenser, and re-bubbled into a precipitation column containing $Ba(OH)_2$. In order to collect inorganic carbon, the sample is acidified with perchloric acid (50 ML/10 L) and the CO_2 produced is bubbled out of the solution and precipitated as $BaCO_3$ in the precipitation column. When no more inorganic carbon can be stripped out, 5 g of potassium persulphate is added to the vessel and the mixture heated to boiling. These harsh oxidation conditions convert all of the organic carbon to CO_2 which is again collected as $BaCO_3$. The barium carbonate was shipped in glass vials to the Geochemistry Laboratory at the University of Waterloo for analysis

on a VG Micromass Mass Spectrometer. The precision of the analysis is very good, about 0.5 parts per mille.

The results of these analyses appear in Figure 30. From this figure it may be seen that the inorganic ^{13}C becomes heavier from Well C2 to PC2A and the PC2D sample is also heavier than the others. PC2C and PC2E are relatively light as is A22. Unfortunately no inorganic carbon figure is available for W2 or W4 because of tube breakage in shipment. From these results it appears that most biological activity took place in Well C2, PC2C, and PC2E. The organic ^{13}C data are almost a mirror image of the inorganic data, as they should be if oxidation of organic matter is influencing the dissolved inorganic carbon. Well C2, PC2C, and PC2E are relatively heavy with respect to ^{13}C, suggesting a preferential selection of ^{12}C. Unfortunately the results from A22 are somewhat ambiguous. The organic data indicate that more biological activity took place in Well C2 and PC2E than in the other piezometers but the inorganic data do not. The organic ^{13}C is lighter that Well C2 or PC2A but it is equal to PC2C and PC2E. It is most unfortunate that other control values could not be obtained. Despite this ambiguity, it appears as though oxidation of organic matter tends to decrease away from Well C2, which is the primary source of Revert. Chemical data discussed earlier in this chapter do not suggest that any traces of Revert remained by the time this study commenced (much higher carbohydrate values would have been obtained), so it is assumed that the shifts in the ^{13}C content of organic and inorganic carbon were caused by the mineralization of Revert after the well was drilled. These results must be considered as tentative but the technique is very promising.

Another line of investigation into the effects of using Revert on chemical analyses was suggested by an examination of the early inorganic chemistry of all the wells and piezometers installed by Groundwater Branch. A few of these (eg. Well 1, P1B, Well 2, Well 3, Well 4, P4B, PC1A, and Well C3) had very low calcium values, sometimes below detection limits. Calcium values below 10 mg/L are uncommon in prairie groundwaters. A further examination revealed that some of these samples also had elevated sodium and potassium

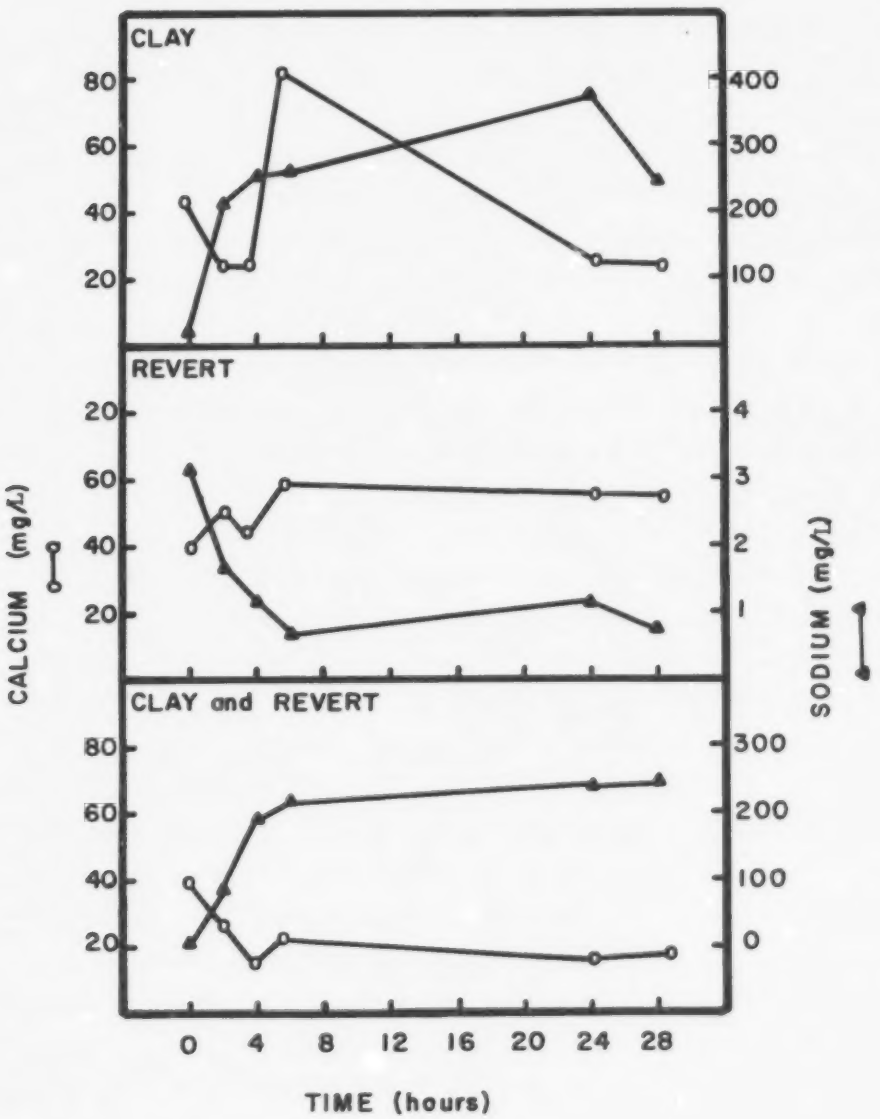
Figure 30. ^{13}C contents of organic and inorganic carbon used to test for the oxidation of revert.



concentrations, suggesting that cations were somehow being exchanged, presumably on clay minerals which are known to be abundant in the spoil material. Bentonite was also used to seal each well and piezometer and is therefore known to be present in large quantities. In order to test this, an experiment was carried out in the laboratory using Revert and driller's bentonite in order to determine whether or not Revert was capable of influencing the cation exchange capacity of the bentonite.

The experiment was carried out as follows: to 400 mL of tap water (unchlorinated containing about 40 mg/L Ca^{++}), 2 g of Revert and 10 g of bentonite were added. This concentration of Revert corresponds to the manufacturer's recommendations for drilling purposes. Two additional flasks containing 400 mL of water were also set up. Two grams of Revert only were added to one and 10 g of bentonite only were added to the other. All the flasks were stirred and 10 ML aliquots were withdrawn at timed intervals from each for sodium, calcium, and hardness analyses. The results are reported in Figure 31. Figure 31 reports calcium and sodium data only for clarity as the hardness results exactly paralleled those for calcium. In the flask which contained clay only, calcium decreased initially, rose sharply, and then declined to a level about half of the starting concentration. Sodium increased steadily from 3 mg/L to nearly 400 mg/L and then declined to 250 mg/L at 28 h. In the flask containing only Revert, the calcium concentration increased only slightly with very little fluctuation. Sodium decreased slowly to less than 1 mg/L after 28 hours from an initial concentration of 3 mg/L. The flask which contained both clay and Revert showed a rapid depletion of calcium (within 4 hours) with very little variability, again to about half the original concentration. Sodium increased equally rapidly and reached a final concentration of 250 mg/L. The exchange of sodium for calcium is clearly dependent upon the presence of bentonite but the reaction proceeds more rapidly and smoothly if Revert is present. Revert did not influence the final concentration of either sodium or calcium compared with clay alone, but it seemed to increase the reaction rate and decrease the variability in concentration of both cations.

Figure 31. The effect of Revert upon the cation exchange capacity of bentonite.



A check of pH revealed a slight drop from 8.52 to 8.08. This experiment was performed at room temperature under aerobic conditions with stirring so fairly rapid reaction rates might be expected. Under cold, static, anaerobic groundwater conditions, this reaction would be expected to proceed much more slowly, if at all. It appears that Revert has a catalytic effect which could be important under field conditions.

Although it was not possible to confirm this hypothesis at Wabamun because of the period of time which had elapsed between the time of drilling and the inception of this project, a more recent case was brought to the investigator's attention in November of 1979 by Groundwater Branch. This involved a well drilled by a private driller in early March 1979, who drilled with Revert but did not use the recommended breaking agents. In August of that year, a complaint was issued to Groundwater Branch because of the offensive odour and taste of the well water which had persisted from the time of drilling. Subsequent analysis showed a high bacterial count, high sodium concentration, and almost no calcium present. Unfortunately, no analysis of total organic carbon was carried out. After the first analysis, the well was pumped extensively and another chemical analysis carried out two days later. This sample contained normal sodium and calcium concentrations and odour had decreased significantly. Based on the laboratory experiment described above and the odour and bacteria problem, it seems fair to say that Revert was the cause of the problem. It appears as though Revert has the capacity to drastically upset the cation chemistry if clay is present (as it usually is under prairie conditions) until it is broken down by microbial action or broken and pumped out. The breaking action of calcium hypochlorite or Fastbreak greatly facilitates the degradation processes and its use is therefore recommended in conjunction with pumping and normal well development. After breakdown has occurred and the material removed, there does not appear to be any lasting effect upon groundwater chemistry.

2.4 DISCUSSION

The investigation of the role of organic geochemistry in the reclamation of coal mines began with an experiment to determine the best way to sample groundwaters. The results of this experiment revealed that the majority of organic compounds in groundwater were stable and not subject to rapid breakdown. This is not surprising as the bulk of dissolved organic constituents have been shown to be complex humic substances by this study and other investigations of the organic content of natural waters. These materials are not easily degraded by either chemical or biological means. As most of the harsh treatments tested were designed to inhibit microbial degradation, it is not surprising that they did not affect the storage of the samples. The nature of humic substances, on the other hand, is to be variable. Chemical properties are known to vary with changes in pH, temperature, light, and precipitation of inorganic substances. It was shown by these experiments that the organic matter does precipitate on the walls of glass containers, and presumably on plastic as well, but that samples could be safely stored for up to one week for the analysis of dissolved organic matter.

Measurements of geochemical conditions in situ were quite successful at Canmore but less so at Wabamun, the principal difficulty being the greater depth of wells and piezometers at the latter site. Despite these problems it was shown that groundwaters tend to be low in oxygen (although rarely anoxic), mildly reducing with respect to Eh, cold, and slightly acidic or neutral in pH. As oxygen was usually present anyway, it was not considered necessary to take any special precautions. Samples were simply kept cool in well sealed plastic bottles and transported to the laboratory for analysis as rapidly as possible.

The initial analytical results confirmed the similarity of groundwater organic chemistry to that of coal in that both are largely made up of humic materials. This is not meant to imply that the composition of coal controls the organic chemistry of groundwater at coal mine reclamation sites as all natural waters follow this trend (Lawrence 1978). Rather, the degradation of plant

material is the origin of these materials and both the formation of coal and the introduction of organic substances into natural waters are part of the natural process of decomposition of terrestrial vegetation. Coal and dissolved humic materials are therefore closely related and interaction between them is not at all inconceivable. Many of these interactions can be described within the realm of organic chemistry by such processes as hydrolysis, polymerization and precipitation. Other interactions are biological in nature and relate to the mineralization of plant material in the soil. These biological aspects will be discussed in more detail in succeeding sections. At this point it is useful to recapitulate the results of the organic analyses of groundwater with reference to spatial and temporal distributions.

The organic geochemistry of groundwater differs between Canmore and Wabamun only with respect to the concentration of some of the parameters measured. The different classes of organic compounds measured are present in approximately the same proportions but concentrations are almost invariably higher at Wabamun. Phenols are conspicuous by their absence (by gross wet chemical techniques at least) at both sites although more sophisticated gas chromatographic techniques would almost certainly be able to detect low concentrations. As this might also be said for a large number of other compounds, more complex analyses were not undertaken. This study has restricted itself to an overview of the classes of organic compounds present and, with the exception of amino acids, carbohydrates, and tannins and lignins, concerned itself with the humic substances which are present in much larger quantities. These are humic acids and "fulvic" acids, the latter of which could only be measured by difference according to the solubility of dissolved organic matter at different pH's. It is probable that at least some of the material counted as fulvic acid by this method is actually something else but more complex analysis would have severely limited the number and variety of other, more important measurements which could be made. Fulvic acid, as measured by this study, comprised much of the total measurement of dissolved organic carbon and the two were invariably significantly correlated ($r = 0.9$).

The samples taken and analyzed from both sites exhibit definite seasonal patterns in the concentrations of all the organic parameters measured. At Canmore, the concentrations of tannins and lignins, carbohydrates, and humic acids were highest in the summer and decreased in the winter. Fulvic acid and dissolved organic matter, conversely, were highest in the winter and decrease in the summer. At Wabamun the concentrations of all parameters were invariably lower in the spring and summer and higher in the fall and winter. As a rule, the levels of all organic parameters were low in the early spring at both sites and increased as the season progressed. This occurred more rapidly at Canmore than at Wabamun and seemed to be triggered by the spring melt. Piezometers were much shallower at Canmore with a correspondingly shallower unsaturated zone and this was thought to explain the more rapid response. Lower concentrations in the spring and summer most probably resulted from the increased biological activity in the soil at that time of year and from the influx of diluting meltwaters.

If all the data at either site are considered at once, no significant relationship between the concentration of organic parameters and depth may be found. If, however, the trend at separate installation nests is examined, concentrations usually decreased with depth. This was not so obvious at Canmore, where only two sites had more than one piezometer, but was frequently observed at Wabamun. The more labile compounds (tannins and lignins and carbohydrates) showed this trend most strongly but humic acid also behaved this way on occasion. This occurred at Control Site 2 at Wabamun as well as at mine site installations.

Cross-section analyses provided interesting insights into the behaviour of dissolved organic compounds at both sites. At Canmore, very little change occurred throughout most of the year, except in the summer when concentrations tended to increase as groundwaters traversed the reclamation site. It would be tempting to conclude that these compounds were inert but the concentration of organic parameters was observed to drop as groundwater emerged from springs at the base of the spoil pile to form Mine Effluent Creek. The exposure of these compounds to increased oxygen, temperature, and light resulted in a decline in concentration. The lush growth

of bacterial slime and macrophytes in this creek supported this observation. Concentrations at Wabamun usually decreased as they travelled through the reclaimed spoil except during March, in the deep wells, and in August, in the deepest piezometers. The delay in the increase in concentration of orgaic compounds in the piezometers (which are completed in the spoil above the bedrock interface) may have been caused by increased biological activity in the shallower spoil material or may only suggest that groundwater in the spoil is not intimately related to that in the bedrock. That organic carbon sources are present in the spoil material and that they can be degraded are shown by the fact that concentrations often jumped between the control installations and the first mine site installation but they usually decreased in a regular manner as the mine site was traversed. This observation is of great importance to both the organic and inorganic geochemistry of the groundwater in the spoil material as the mineralization of organic matter can affect pH and change mineral solubilities (Stumm and Morgan 1970). This topic will be returned to in later sections.

Amino acids in groundwaters result from the degradation of plant material. They occur in the free form and in polymeric form more commonly known as proteins. The latter are more difficult to degrade because they must be hydrolyzed before they can be ingested by microbiological agents or before they can participate in other chemical reactions. Free amino acids can condense to form proteins or hydrolysis may take place depending upon local chemical conditions. They may also react with humic materials (de Haan and de Boer 1978) and form important sources of nutrition to a wide variety of micro-organisms. The concentration of amino acids was similar at both sites, usually less than 100 μg/L. The relative abundance of both free and combined amino acids varied according to season but glutamic acid and aspartic acid emerged as the most abundant and, by inference, the most stable amino acids at both sites. The fact that they are there at all indicates that a nutritive base for heterotrophic micro-organisms exists in groundwaters and the presence of bacteria in large numbers (see Chapter 4) suggests that biological activity may be important in the spoil material.

The use of Revert in the rotary drilling operations at Wabamun does not seem to have had a lasting effect upon the organic chemistry of the groundwater in the vicinity of wells and piezometers. Studies with ^{13}C suggest that an increased amount of biological activity took place after the wells were drilled because of the large amounts of carbohydrates added but the concentrations of organic materials and the numbers of bacteria present had declined to background levels by the time this study began. Initial total organic carbon measurements taken by Groundwater Branch were very high in many wells and piezometers but they declined after several months. Revert seems to have a catalytic effect upon the cation exchange capacity of the bentonite used to seal the casing above the well screens. Both field and laboratory observations indicate that calcium concentrations can be severely depressed and that sodium levels increase correspondingly. This effect was observed to decline with decreasing total organic carbon at Control Site 2 according to data collected by Groundwater Branch. The effects of Revert upon both organic and inorganic geochemistry can be minimized if breaking agents are used and the remaining organic material is pumped out during normal well development. If these precautions are observed, Revert can be used for studies of this sort but the use of dry methods of drilling such as augering are preferable whenever possible.

3. MICROBIOLOGICAL INVESTIGATIONS RELATED TO COAL MINING

3.1 INTRODUCTION

Bacteria and fungi are found in soil and deeper geological formations although most microbiological activity takes place in shallow soil horizons. Below the aerobic zone, fungi are usually absent but anaerobic and facultative bacteria are common. These bacteria may be broadly divided into two major classes, heterotrophic and autotrophic. The former derive energy from the oxidation of detrital organic matter and the latter from the oxidation of various mineral species. Even autotrophic bacteria are partially dependent upon the presence of some organic matter as it serves as an alternate electron acceptor and also has some nutritional importance (Matin 1978) as well. These two major classes of bacteria are introduced separately below.

3.1.1 Heterotrophic Bacteria

The ability of micro-organisms and even some invertebrates to use organic compounds as a food substrate is well known. The role of natural organic compounds, which originate from plant decomposition, in the nutrition of soil and aquatic organisms is less well understood and,in the field of groundwater research, very little has been done at all. The organisms which exist in groundwater, however, originate in the soil and are often common to surface water bodies, so a review of the information available from soil and freshwater research is useful to the investigation of organic matter and micro-organisms in deeper strata and groundwater.

Sepers (1977) has discussed the ability of invertebrates, algae, bacteria, and fungi to use natural dissolved organic matter and has concluded that bacteria are the most important group involved. Plants are autotrophs and the ability of certain algae to utilize organic compounds in the dark does not greatly influence the detritus food chain. Invertebrates are similarly either predatory, herbivorous, or interested in much larger particles for ingestion, and the occasional supplement of dissolved material does not constitute a major trophic pathway. Fungi are considerably more important in this regard, but even they do better when engaged in

the breakdown of solid substrates such as leaf material. Iverson (1973) found that fungal biomass was much lower than that of bacteria even on decomposing beech leaves in a small stream in Denmark although Kaushik and Hynes (1971) concluded that fungi are a major source of protein for invertebrates. Fungi are best known with regard to their ability to degrade cellulose and lignin in shallow soil horizons and they may compete with bacteria for dissolved organic matter. The larger size of fungal spores and conidia, however, make downward migration through the soil difficult and the lack of oxygen and solid organic substrates impose restrictions on fungal growth. Bacteria, on the other hand, are much smaller, more mobile, and their diverse populations possess the ability to degrade almost any organic substrate (Wistreich and Lechtman 1980). Throughout this study, bacteria were the only micro-organisms found in free groundwater.

The concentrations of dissolved organic matter normally found in ground and surface waters from natural sources is low (Wallis et al. in press). Natural bacteria have adapted to these low substrate concentrations and this has made culturing them on the normal enriched media difficult (Romanenko 1979). According to this author, culture media prepared from natural materials are superior to enriched media for the growth of natural micro-organisms. Stabel and Overbeck (1979) have demonstrated the ability of certain strains of bacteria to degrade refractory organic material such as humic and fulvic acids which were separated from lake water by Sephadex filtration. They found that bacteria would preferentially take up small molecular weight molecules and 'oligomeres' (molecular weight 400-600) and that macromolecules were much more resistant to attack. If glucose was also added, co-metabolism of easily consumable (small) compounds and macromolecules could occur. The rate of decomposition was slow, extending over several months. Similar results were found by de Haan (1977).

Hackett et al. (1977) measured the uptake rate of ^{14}C labelled lignins in soil and found an average turnover time of 884 days. Crawford, Floyd, and Pometto (1977) found that up to 30% of natural lignocellulose was degraded after 40 days although the rate of degradation was dropping toward the end of the experiment. These

authors also concluded that the pattern of degradation was the same for both soil and water micro-organisms. Grant (1976) showed that the fungus Penicillium adametzi could also degrade condensed tannins at a rapid rate (2 days) under optimum laboratory conditions. Mathur (1969) found that several other fungi could convert fulvic acid to humic acid and that Poria subacida could degrade fulvic acid itself. Growth on humates had been previously shown by Mathur and [illegible]l (1967) by the fungus Penicillium frequentans. Although these compounds are resistant to microbial attack, it is evident that they can be at least partially broken down in a period of time less than one year.

Several workers have also demonstrated the ability of microorganisms to degrade organic substrates not normally found in significant quantities in the natural environment. Robinson, Hendzel, and Gillespie (1973) found turnover times ranging from 8 to 950 hours for ^{14}C labelled simple organic acids. They tested lactic, pyruvic, fumaric, malic, acetic, succinic, glycolic, citric, and formic acids and found in West Blue Lake, Manitoba, that bacterial populations were directly related to substrate disappearance. Soyupak, Farquhar, and Sykes (in prep.) found that leachate from a landfill site was rapidly degraded by soil micro-organisms. The organic load of 11.6 g/L was almost entirely degraded after 60 days in a soil column set up in the laboratory. A considerable amount of work has also been done to demonstrate the degradation of petroleum products and even toxic pesticides (Wistreich and Lechtman 1980).

The mineralization of organic compounds is rarely accomplished all in one step by one organism in nature. Rather, the decomposition products of one organism may serve as a substrate for another. This has been demonstrated by Cappenberg (1979) in the anaerobic mineralization of natural organic matter. He states that at least two physiologically different populations of bacteria must be present for a complete conversion to CO_2 and CH_4 under anaerobic conditions. In the first stage, refractory compounds such as cellulose and chitin are converted mainly to fatty acids and to hydrogen gas by fermentation and hydrolysis. In the second stage, the end products of the metabolism of the first stage are converted to CO_2 and CH_4. In the case of methane production, a third

group of organisms may be involved which converts fatty acids and alcohols to compounds which can be degraded by H_2/CO_2-fermenting methanogenic bacteria (Cappenberg 1979). Fleischer and Gahnstroem (1979) were also able to show that the extra-cellular products resulting from the uptake of glucose were in turn metabolized in sediments. The heterogeneity of both aquatic and soil microbial populations offers a versatility which allows for the eventual decomposition of almost any organic molecule. Mathematical models describing this chain of events have been applied with some success by Clesceri, Park, and Bloomfield (1977) for aquatic ecosystems and by Smith (1979) for soil. At the present time, however, only conceptual models are possible for the degradation of natural organic material in deeper strata and groundwater. There is a belief among many microbiologists that micro-organisms can degrade any organic molecule given the right conditions and enough time although certain pesticides, detergents, and plastics have defied this hypothesis (Wistreich and Lechtman 1980). The new prospects for the genetic engineering of bacteria may lead to organisms capable of decomposing even these unpromising substrates. An abbreviated bibliography of papers dealing with the degradation of natural and introduced organic compounds in water has been provided in Table 24.

3.1.2 Autotrophic Bacteria

The relation of autotrophic microbiology to inorganic water quality problems associated with coal mining is principally related to the oxidation of iron and oxidation and reduction of sulphur. These microbial activities cause inorganic chemical problems such as acidification or well screen clogging under the appropriate conditions. A thorough review of all the literature pertaining to these topics is outside the terms of reference of this report and would require a lengthy document by itself. For this reason the review presented here will restrict itself to information available which is directly applicable to western coal mining.

3.1.2.1. Iron Bacteria. Iron may be transformed by micro-organisms in a variety of ways. Some bacteria may oxidize ferrous iron to the

Table 24. Abbreviated bibliography of papers dealing with the uptake of natural organic matter in ground and surface waters.*

Natural Dissolved Organic Matter

Sepers (1977), Tison and L'Ingg (1979), Pitter (1976), Romanenko (1979), Stabel, Moaledj and Overbeck (1979), Varma, Weekes and Calvert (1975), Fleischer and Gahnstrom (1979), Clarke (1980), Moaledj and Overbeck (1980), Fenchel and Jorgensen (1977), Bick and Mueller (1973), Bertoni and Callieri (1978), Lock and Hynes (1975), Wallis et al. (in press), Cappenberg (1979), Smith (1979), Clesceri, Park and Bloomfield (1977).

Tannins and Lignins

Mahadevan and Muthukumar (1980), Haider, Trojanowski and Sundman (1978), Hackett et al. (1977), Grant (1976), Crawford et al. (1977).

Carbohydrates, Amino Acids, and Other Simple Organic Compounds

Hall, Kluber and Yesaki (1972), Wright and Hobbie (1966), Gude (1978), Wright (1978), Stanley and Stally (1977), Hobbie (1973), Egglishaw (1972), Hofsten and Edbert (1972), Tribe (1961), Robinson et al. (1973), Fleischer and Gahnstrom (1979).

Humic and Fulvic Acids

de Haan (1977), Mathur (1969), Mathur and Paul (1967).

Petroleum and Hydrocarbons

Hill (1967), Jones (1969a), Liu and Dulka (1973), Humphrey and Witt (1979), Roques, Masbermat and Tsacoyaunis (1976), Schaeffer et al. (1979).

Organic Nutrition of Chemolithotrophic Bacteria

Matin (1978)

Landfill Leachates

Soyupak, Farquharand and Sykes (in preparation).

* The full references may be found under 'Literature Cited.'

ferric state, causing ferric hydroxide to precipitate (Glover 1975; Tuovinen and Nurmaiho 1979; Valkenburg, Christian and Green 1975). These include species of the genera Thiobacillus, Gallionella, Crenothrix, Leptothrix, Pediomicrobium, and Sphaerotilus. These bacteria are often found encrusted in precipitated ferric hydroxide (Tuovinen and Nurmaiho 1979) although it is not known for certain that these organisms have derived energy from the oxidation of iron (Levy, Campbell and Blackburn 1973) or if the deposits are caused by the chemical environment in which they live. The ferrous ion, which is very soluble in water, predominates below pH 5 and the relatively insoluble ferric ion is favoured above pH 6. If the Eh falls below 0.2 volts, the ferrous ion is similarly predominant (Stumm and Morgan 1970). These chemical constraints often make it difficult to distinguish between microbiological and purely chemical effects.

The major sources of iron found in conjunction with coal mining activities are pyritic minerals, usually FeS_2. While these minerals may be oxidized and dissolved by purely chemical pathways, the rates of reaction under ordinary environmental conditions are low. The presence of bacteria capable of deriving energy from the oxidation of ferrous iron greatly speeds up the process (Alexander 1977). The best known of these is the autotrophic Thiobacillus ferrooxidans, formerly called Ferrobacillus ferroxidans, which has become famous in conjunction with the acid mine drainage problems encountered in the Eastern United States. This organism has the ability to obtain energy from the oxidation of both ferrous and sulphide ions derived from pyrite. A by-product of this oxidation is sulphuric acid, causing a very low pH in mine drainage waters which are unbuffered. The optimum pH for the growth of this organism is from 2.0 to 3.5 and these acid conditions also favour the dissolution of many trace metals from overburden materials. The energy derived from iron oxidation may be used by the organism to reduce CO_2 to usable organic compounds (Dugan and Lundgren 1965) and permit cell growth. It has been assumed until recently that this organism was not important in western coal mines because of the neutral-alkaline nature of overburden materials but evidence put forward by Harrison (1978), Olsen and McFeters (1978) and Olson, Turbak, and McFeters (1979), suggests that this may not be true.

Research carried out in Montana and in Missouri by these authors have shown that this organism is common at the minesites they worked at and that it may be responsible for increased concentrations of iron and sulphate in ground and surface waters. Dissolved iron cannot be present in large quantities under alkaline conditions unless oxygen is not present and Eh is below 0.2 volts. Under these conditions ferrous iron may be dissolved in large quantities, usually as $Fe(HCO_3)_2$ (Stumm and Morgan 1970). This was found to be the case in Well 4 at the Whitewood Mine in this study and has been commonly reported in the United Kingdom (Glover 1975). As this organism is also important in the consideration of sulphur, it will be further dealt with below.

Organic matter is known to bind with iron (Kent and Hooper 1965). As many heterotrophic bacteria and fungi attack soluble organic iron salts, inorganic iron may be liberated. If the chemical environment is appropriate, the iron may be precipitated from solution (Alexander 1977).

The growth of micro-organisms often results in the lowering of pH and the removal of oxygen, causing a drop in the Eh of the solution. Acidity increases by the production and release of organic acids as well as by the solution of CO_2 (forming carbonic acid in water) resulting from heterotrophic activities. Extensive activity by aerobic organisms in a medium not directly connected to the atmosphere or containing photosynthetic organisms can lead to anoxic conditions. The combination of acidic and reducing conditions greatly increases the solubility of iron minerals by reducing the iron moiety to the ferrous state. This is also true for other trace metals and common salts. These are the conditions which are often encountered in groundwater (Champ, Gulens, and Jackson 1979).

3.1.2.2 Sulphur Bacteria. The sulphur cycle in the soil is aided at every stage by sulphur bacteria. Mineral sulphides and organic sulphur compounds may be oxidized to sulphate in the presence of oxygen. This sulphate is then available to plants and other soil organisms as a nutrient. Sulphate may in turn be reduced under anaerobic conditions by other bacteria to hydrogen sulphide or back

to mineral sulphides. The reduction of sulphate requires an additional energy source in the form of organic matter. These reactions also serve to change the concentration of sulphate in groundwater and, under the appropriate conditions, cause the production of hydrogen sulphide which lowers the pH and gives off a characteristic "rotten egg" odour.

Sulphur oxidizing bacteria fall into three main groups: the chemoautotrophic sulphur bacteria (Thiobacteriaceae, Beggiatoaceae, and Achromatiaceae), the photosynthetic sulphur bacteria (Thiorhodaceae and Chlorobacteriaceae), and certain heterotrophic microorganisms including some actinomycetes, bacteria, and fungi. Of these, only the Thiobacilli and certain heterotrophs are generally involved in sulphur oxidation in soils (Wainwright 1978). Heterotrophic bacteria including Arthrobacter spp., Bacillus spp., Flavobacterium spp., and Pseudomonas spp. have been shown to oxidize sulphides in vitro but their importance in soils is not known. Various actinomycetes and fungi also have this ability but their significance is in doubt. By far the commonest and most active group is the Thiobacilli (Wainwright 1978) although Alexander (1977) maintains that the heterotrophic bacteria may be dominant in the presence of large amounts of organic sulphur.

The commonest species of the genus Thiobacillus are listed in Table 25 along with the environmental requirements and the reactions they catalyze. In general, thiosulphate, elemental sulphur, or inorganic sulphides are oxidized to sulphate. Although these bacteria are generally considered to be chemoautotrophic, Matin (1978) has shown that a variety of organic compounds may also stimulate growth. Smith and Kelly (1979) have shown that this ability confers a selective advantage in the chemostat. Thiobacillus ferrooxidans may also oxidoze the iron component of pyrite (FeS_2) to obtain energy (Dugan and Lundgren 1965, Arkesteyn 1979). Both this organism and Thiobacillus thiooxidans produce sulphuric acid and have an optimum pH of about 3.0, revealing them to be the bacteria responsible for the acidification of unbuffered waters. Because western coal mines are based in carbonaceous rock, they have not been considered to be prone to acidification problems and low

Table 25. The environmental requirements and reactions catalyzed by several common sulphur bacteria in soil.

Organism	Oxygen Tolerance	Trophic Status	pH Optimum	Reaction Catalyzed
novellus	obligate	heterotrophic	neutral-alkaline	$Na_2S_2O_3+2O_2H_2O$ $_2NaHSO_4$
thioparus	oblitate aerobe	chemoautotroph	neutral-alkaline	$5Na_2S_2O_3+4O_2+H_2O$ $5Na_2SO_4+H_2SO_4+4S$ and $NA_2S_4O_6+Na_2CO_3+1/2O_2$ $2Na_2SO_4+2S+CO_2$
thiooxidans	obligate aerobe	chemoautotroph	2 - 3.5	$S+O_2+H_2O$ H_2SO_4
denitrificans	facultative	chemoautotroph	neutral-alkaline	$5S+6KNO_3+2H_2O$ $K_2SO_4+KHSO_4+3N_2$
ferrooxidans	obligate	obligate	2 - 3.5	oxidizes either ferrous or sulphur salts
desulfovibrio spp.	obligate anaerobe	heterotrophic	above 5.5	e.g. $R\text{-}CHOH\text{-}R^1+MgSO_4$ $H_2+R\text{-}R^1+CO_2+MgCO_3+H_2O$
desulfotomaculum spp.	obligate anaerobe	heterotrophic	above 6.0	same as *desulfovibrio* but a variety of organic substrates may be used

pH has not been commonly encountered. Olson and McFeters (1978) and Olson, Turbak and McFeters (1979), however, have reported the presence of Thiobacillus ferrooxidans at the Decker Coal Mine in Montana. This organism is presumed to exist in small pockets where the pH can be reduced and, although the pH of groundwaters was not observed to drop, mine drainage waters in No Name Creek were observed to have a pH of only 2.8. In addition the buffering of any acid produced in groundwaters will involve the further dissolution of elements such as calcium which will raise the hardness of the water and contribute to total dissolved solids. As far as can be determined, this is the first time that acidification reactions have been reported in conjunction with western coal mining. Harrison (1978) has reported the dominance of Thiobacillus ferrooxidans in experiments with coal spoil material from a Missouri coal mine. The phenomenon has also been extensively documented in the unbuffered waters of the eastern United States.

Various species of the genera Desulfovibrio and Desulfotamaculum are the commonest sulphur reducing bacteria although species of such bacteria as Salmonella and Proteus should also be noted in this regard (Wistreich and Lechtman 1980). The environmental requirements and the reactions catalyzed by the former two are listed in Table 25. Under anaerobic conditions sulphate is reduced, usually to hydrogen sulphide but iron pyrites (insoluble) may also be produced. Sulphate is used as an electron acceptor and an organic compound, such as lactate, functions as an electron donor (Nedwell and Abram 1979). The reaction appears to be most strongly affected by temperature (Nedwell and Abram 1979) and less so by the concentration of electron donor. Both carbon dioxide and hydrogen sulphide are produced and these tend to reduce the pH of the solution by the production of carbonic acid by the former and by the dissociation of the latter.

The media used for the isolation and enumeration of sulphate reducing bacteria have been reviewed by Mara and Williams (1970) and the taxonomy of the Desulfovibrio group is discussed by Postgate and Campbell (1966). Although the activities of these organisms have the potential to remove troublesome concentrations of sulphate from groundwaters, the attendant production of hydrogen

sulphide creates an objectionable odour in water supplies. This can be alleviated, however, by aeration. Sulphate reducing bacteria may also be involved in the anaerobic precipitation of calcium carbonate by their reducing action on calcium sulphate (Doetsch and Cook 1973).

3.2 METHODS OF MICROBIOLOGICAL SAMPLE COLLECTION AND ANALYSIS

3.2.1 Direct Counts Using Epi-fluorescence

All wells and piezometers were bailed out and water samples for the direct counts of bacteria were filtered in the field through sterile, .22 μ Nuclepore polycarbonate membranes with a sterile Millipore filtration apparatus. Sample size varied from 1 mL to 10 mL, depending upon the amount of silt present. The membranes were secured to 5.5 cm Whatman #1 filter paper circles with rubber cement and were placed in small plastic petri dishes. These contained a small wad of cotton wool soaked in 0.5% glutaraldehyde to fix the bacterial cells until they could be observed upon return to the laboratory (Geesey et al. 1978). They were stained with acridine orange (0.01% solution in 0.1 M potassium phosphate buffer, pH 7.5) and counted using a Zeiss Photomicroscope II equipped for epi-fluorescence. The illumination source was an HBO 200 Watt burner with the following filter combination; excitation - KP 490, LP 455, beam splitter - LP 510, barrier filter LP 520. Bacteria fluoresced orange or green and were counted with a hand counter. This method was modified from the original method of Zimmermann and Meyer-Reil (1974).

3.2.2 Plate Counts

The estimation of bacterial populations by plate count methods is very much dependant upon the growth medium selected. For this study, three media were evaluated; nutrient agar, brain-heart infusion agar, and tryptone-glucose-yeast (TGY) agar. Although all of them supported growth from various wells and piezometers, brain-heart infusion agar diluted to one-tenth the normal concentration almost always produced the highest number of colonies. Samples to be examined for viable counts were collected in autoclaved 125 X 16 mm pyrex culture tubes and transported to the laboratory in

an insulated cooler containing ice. A total viable count was obtained by culturing dilutions made with sterile 0.85% saline on brain-heart infusion agar (3.8 g/L). Agar plates were inverted and incubated in the dark at 5°C for two weeks. Counts were made using a Luxo lamp magnifier and a 1 cm grid outline. This method is only effective for heterotrophic bacteria and is an underestimate of the total population because no one medium is suitable for the growth of all types of heterotrophic bacteria.

3.2.3 Sulphate Reducers

The presence of hydrogen sulphide at several sites at Wabamun and in P6 at Canmore suggested the presence of sulphur reducing bacteria. These bacteria were cultured on Oxoid Iron Sulphite Agar . To prepare the medium, it was first necessary to boil it to remove all oxygen and then it was autoclaved at 121°C for 20 minutes. It was then flushed with CO_2 gas and 7 mL of filter sterilized 7.5% ascorbic acid and 7.5% sodium thioglycolate were added to 500 mL of the agar. Five mL of resazurin solution (0.02 g in 2 mL of 5N NaOH and diluted to 50 mL with filtered deionized water) were added to the media as a redox indicator. A 1 mL water sample was aseptically pipetted into autoclaved culture tubes (125 X 16 mm) and the cooled agar was poured into the tubes leaving about 2 cm at the top. The tubes were inverted six times to ensure mixing of the sample throughout the medium. After solidification of the medium, autoclaved molten agar was poured into each tube until full, screw caps put on, and they were incubated at 5°C in the dark. After 28 days incubation, all tubes were examined for the presence of black, circular colonies which were recorded as evidence for the presence of sulphur reducing bacteria. This method does not permit quantification of these bacteria, it merely records their presence or absence.

3.2.4 Iron Oxidizers

An attempt was made to isolate and culture iron oxidizing bacteria using Aleem's modification of the original method of Silverman and Lundgren (1959). The low pH of this medium inhibits the growth of all but the most acidophilic bacteria and growth of

Ferrobacillus spp. is favoured. Flasks containing Silverman and Lundgren's 9K salt medium were inoculated with bacterial slime from Canmore Creek known to contain iron oxidizing bacteria (T. Ladd - pers. comm. telephone conversation, Feb. 2, 1980) and with water from P2A at the Canmore site. No growth could be observed in this medium even though the presence of the bacteria was strongly suspected. Further trials were impeded by the heavy precipitation of iron salts in the medium which rendered the observation of turbidity impossible. These salts were also impervious to microscopic examination with acridine or Gram's stain. It was eventually discovered that these salts could be broken up and partially redissolved to reveal the bacterial cells but, unfortunately, no results were obtained for this project.

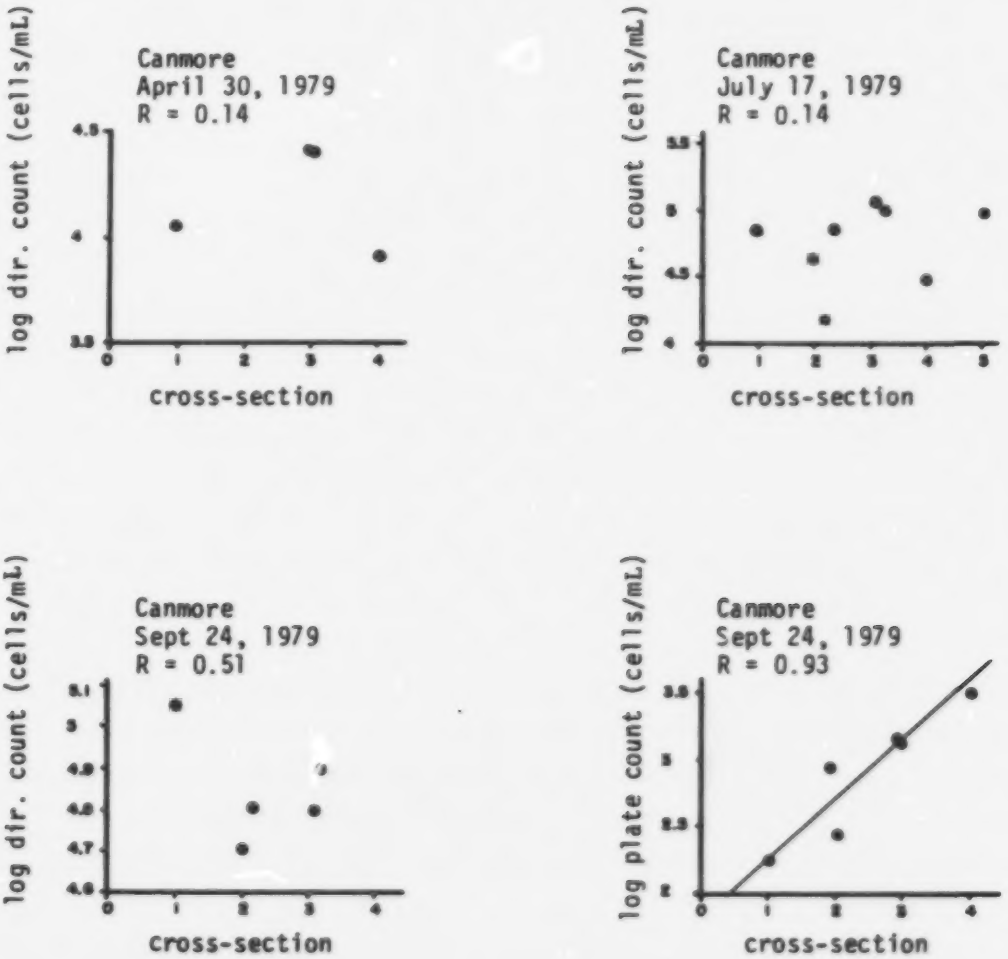
3.3 RESULTS

3.3.1 Direct Counts and Plate Counts

Considerable numbers of bacteria were found at both Canmore and Wabamun in ground and surface waters. No significant correlation could be found between bacteria counted by direct observation and those counted by culturing methods either at individual sites or with all the data taken together. This is presumably because plate counting methods only count heterotrophic bacteria (and not all of these depending upon the growth medium selected) and direct methods count all types of bacteria indiscriminantly, even if they are dead. Cell concentrations ranged from between a few hundred cells/mL to several million but direct counts were invariably higher than plate counts. The concentrations found by either method could not be significantly correlated with depth at any location (the regression coefficient, r, never exceeded 0.5). The range of concentrations found by both methods was similarly unaffected by the time of year of the sample.

Figure 32 reports bacterial data counted by both methods from both sites as they occurred along the cross-sections used in Chapter 2 at Canmore on April 30, July 17, and September 24, 1979. Unfortunately, no plate counts are available for the April 30 sample. Bacteria counted by the direct method did not show any pattern of distribution across the mine reclamation site on any of

Figure 32. Microbiological data from Canmore.



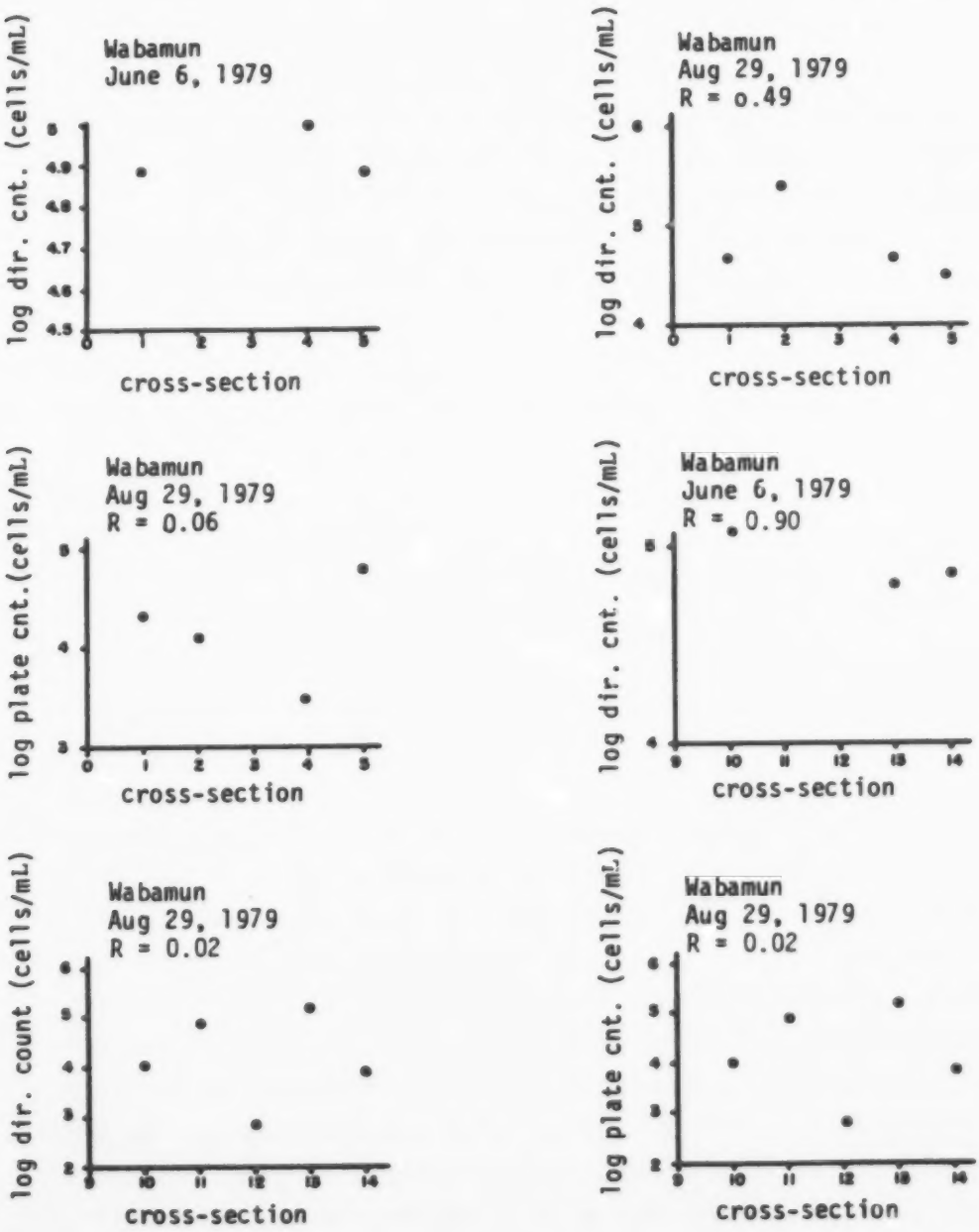
the three sampling dates. Bacteria counted by the plate method showed a tendency to decrease from the control piezometer (P1) through the site on July 17. At this time, dissolved organic matter also decreased across the site (see Figure 18), the only time when this trend was observed. On September 24, the heterotrophic bacteria counted by the plate method increased consistently across the mine site. At this time, there was a tendency for dissolved organic matter to increase also (Figure 18), suggesting that a relationship exists between dissolved organic matter and heterotrophic bacteria. Tannins and lignins also followed this pattern although the other measured organic parameters did not.

Bacterial data from the cross section across the Wabamun mine site are plotted in Figure 33 for samples taken on June 6 and August 29, 1979. At this site no relationship could be detected across the mine site on either date. Bacteria were present in numbers very comparable to those found at Canmore. Although these data do not suggest any relationship between dissolved organic matter and bacteria populations, it is noted that dissolved organic matter did not vary to any extent across the reclamation site at Wabamun on those dates either (Figures 27 and 28).

3.3.2 Sulphur Reducing Bacteria

A number of samples were taken on different occasions in order to test for the presence of these bacteria. Unfortunately the method was developed rather late in the project, so a number of installations at Wabamun were missed. The presence of these bacteria was detected at P6 at Canmore on September 24, 1979 but could not be found at any other site there (all piezometers were checked at Canmore). At Wabamun, sulphur reducing bacteria were found in Well 4, P4B, and PC2B but not in PA18 or Well 7 on August 29, 1979. On November 14, 1979, they were detected in PC2B and P4B again but not in Well 4 this time. P4C and PC2D also contained these bacteria although Well C2, PC2A, PC2C, PC2E, PA22, and P4A did not. The presence of H_2S could be detected by smell at many of these installations so it is probable that sulphur reducing bacteria were more widespread than these results suggested. As these are strictly anaerobic bacteria, they are subject to death by aeration during

Figure 33. Microbiological data from Wabamun.



transportation to the laboratory which may be responsible for some of the negative results.

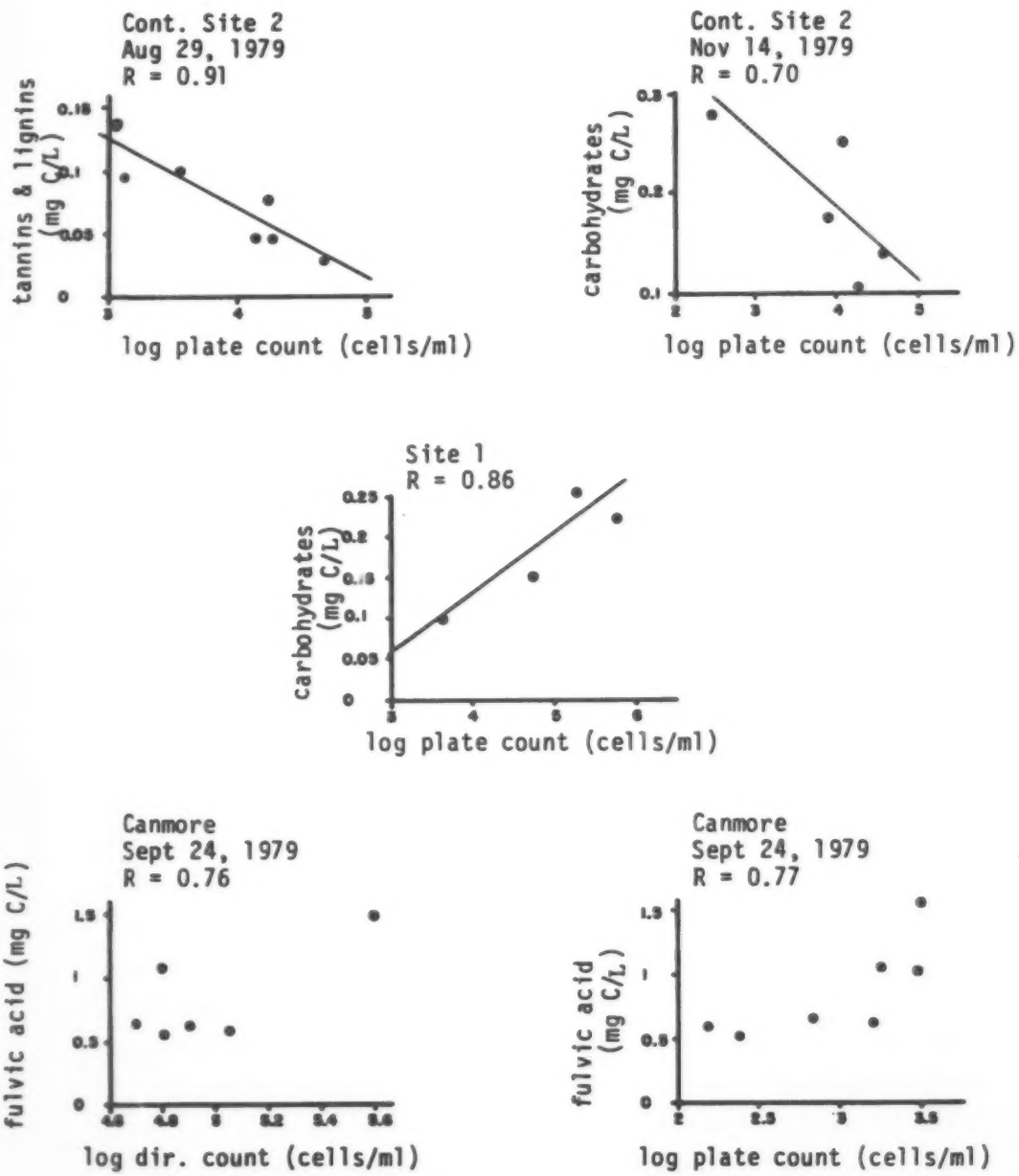
3.4 DISCUSSION

The measurement of bacteria in natural water samples yields results which depend very much upon the method employed. Direct counts are usually considered to overestimate the population because the method is incapable of distinguishing between living and dead bacteria. Plate counting methods are similarly considered an underestimate because no universal medium exists which will support the growth of all types of heterotrophic bacteria equally well. Despite these difficulties, the difference between populations measured with the two methods gives an estimate of the autotrophic bacteria present. The results reported in Figures 32 and 33 clearly indicate that there is often a wide discrepancy between the population estimates given by the two methods and this suggests that autotrophs are well represented in these groundwaters. The results reported in Section 3.3.2 bear this out.

That the populations of heterotrophic bacteria should be related to the concentration of organic compounds present is intuitively easy to accept but this phenomenon is difficult to observe. All of the data from both sites were used in an attempt to discover any relationships between the various organic parameters measured and the populations of bacteria measured by direct and plate techniques. None were evident at either site. From there the analysis proceeded to considering the data from installation nests at Wabamun and all the piezometers together at Canmore on separate dates. The results of most of these analyses were negative (and are not shown in figures here in the interest of brevity) but a few relationships were detected. These are reported in Figure 34. These relationships all had a correlation coefficient greater than 0.7 and included at least four data. Of these only the relationship between tannins and lignins and heterotrophic bacteria found at Control Site 2 on August 29 can be considered as significant.

In order to understand why the concentrations of organic matter are not usually related to bacterial populations it is necessary to consider several points. It has been shown that the

Figure 34. Relationships between bacteria in groundwater and dissolved organic compounds at Wabamun.



uptake of simple, labile organic compounds is much faster than that of more complex, refractory compounds (Stabel et al. 1979; Smith 1979). If a labile compound is added artificially, some co-metabolism of more refractory compounds may also occur (Stabel et al. 1979) but the latter compounds persist. This explains the observation that most of the dissolved organic matter in natural waters consists of large molecular weight humic and fulvic acids which are refractory in nature and that more labile compounds (carbohydrates, amino acids and simple organic acids) are scarce. If more labile compounds are added to a natural ecosystem a rapid response may be observed in bacterial populations until the substrate is largely used up. A slow decline to low population levels and a switch to other substrates then occurs under these, essentially starvation, conditions. This situation represents an equilibrium between low inputs of labile material from plant decomposition, the release of extracellular products, or the release of simple compounds from humic and fulvic acids by chemical means and a heterogeneous bacterial population. The degradation of labile material also contributes to the production of large molecular weight humic and fulvic acids as the by-products react with each other and aggregate (Clesceri et al. 1977). Some of this material may be in turn degraded by other bacteria so that a dynamic equilibrium results which is characterized by stable concentrations of dissolved organic matter and slowly fluctuating microbial populations.

If more labile compounds become available seasonally with fluxes in groundwater movement, the relative magnitudes of the concentration increases are probably not very large. Bacterial cells observed from groundwater samples by direct microscopy are always very small. The same cells increase in size dramatically when cultured on a rich medium such as brain-heart infusion and a certain amount of growth must occur before rapid reproduction results. In the natural system the inputs of labile organic matter are probably not great enough to permit a rapid rate of growth and so populations react slowly (Varma et al. 1975). In addition to relatively low inputs of labile organic matter, nutrients such as NO_3 and PO_4 are usually not abundant and impose limitations to growth (Smith 1979).

These factors are all part of a very complex ecosystem consisting of a heterogeneous population of bacteria which react in differing ways to changes in organic loading (Stabel et al. 1979; Fleischer and Gahnstrom 1979; and Cappenberg 1979). Organic molecules are partially degraded, the by-products recombine, further degradation takes place, and bacterial populations respond slowly. In short, a dynamic equilibrium exists which is difficult to interpret by such simple measurements as the concentration of broad classes of compounds and wide groups of micro-organisms at lengthy and irregular time intervals.

In the light of the discussion above it is suprising that any relationships at all were found between bacterial populations and organic concentrations. It is possible that these relationships indicate that a change was taking place at the time the sample was taken in response to a change in the loading of organic compounds or the availability of nutrients. If this sort of relationship indicates that the system is responding to a change and that equilibrium has been upset, it may be possible to exploit this phenomenon to both understand the dynamics of organic degradation and to recognize the effects of organic pollution. If this is true, a fascinating and profitable line of research may be opened up.

4. LEACHING OF COAL AND SPOIL MATERIAL IN THE LABORATORY

4.1 INTRODUCTION

In order to more fully understand the relationship of coal in spoil material to organic and inorganic groundwater geochemistry, leaching experiments were carried out in the laboratory. These were undertaken in the hope that the interpretation of data collected in the field would be made easier and that some of the conclusions made from field sampling would be confirmed. The materials used all came from the Wabamun site and the specific objectives of the leaching experiments were as follows:

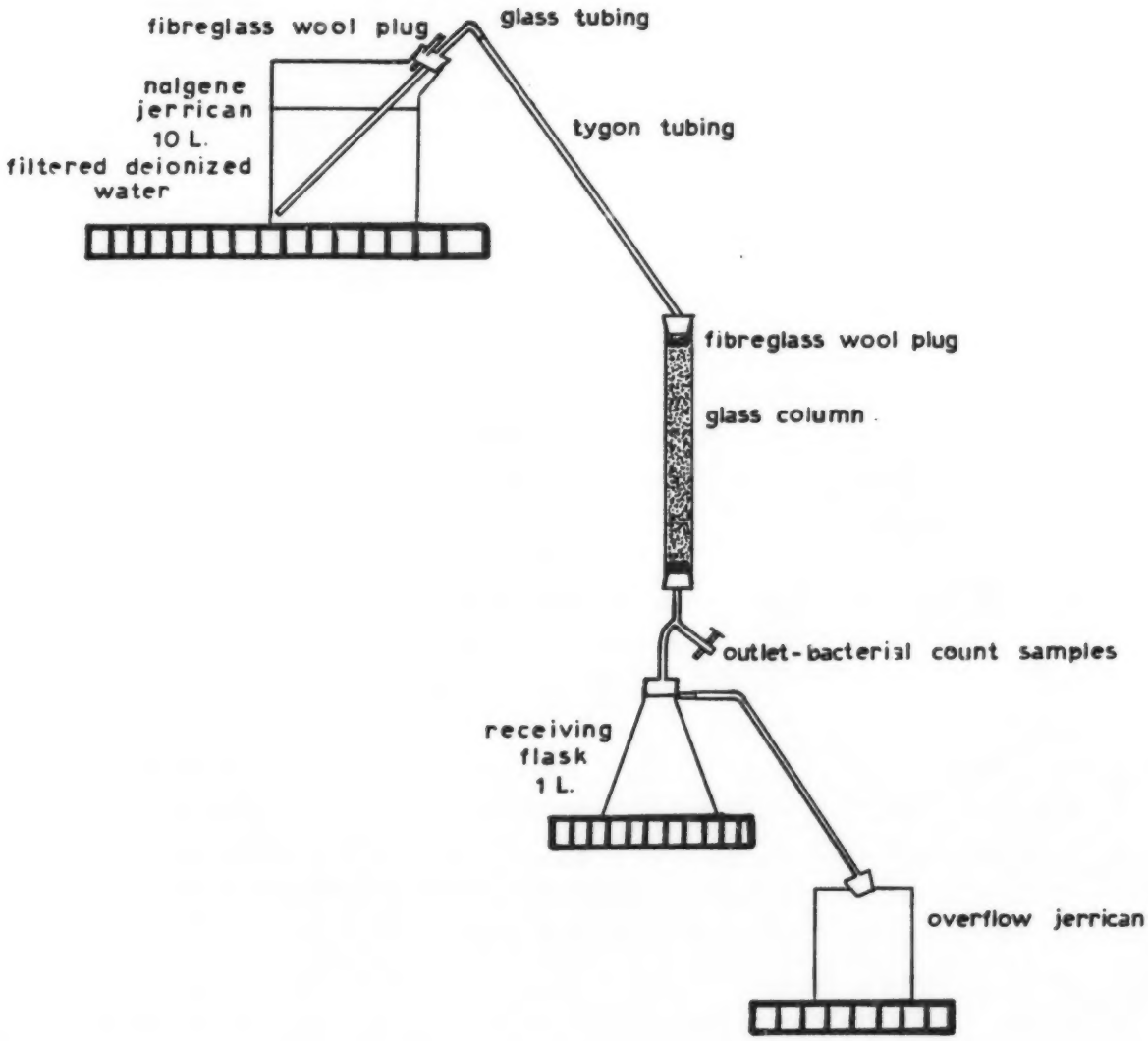
1. to investigate the organic chemistry of coal by itself under septic and aseptic conditions;
2. to discover the influence of varying amounts of coal mixed with spoil material on bacterial populations, organic chemistry, and inorganic chemistry; and
3. to test the effect of the addition of the organic drilling mud 'Revert' to the microbiology and geochemistry of the leachate.

Leaching columns made of glass tubing were set up in order to simulate the passage of groundwater through various geologic materials. Filter sterilized deionized water was used for leaching. Wabamun coal was taken from the main dump at the thermal plant and overburden material was sampled from the high wall at the West Pit. Care was taken to ensure that the overburden was not contaminated with coal remains. This material was taken from a depth approximately 10 m below the original ground surface and may be described as a poorly sorted sand mixed with small amounts of silt and clay. The details of the methods employed are given below.

4.1.1 Methodology

Glass columns 3 cm in diameter were mounted on a framework and placed in a cold room maintained at 5°C in darkness (Figure 35). All glassware, tygon tubing, and nalgene jerricans were washed with Sparkleen detergent in hot water, rinsed with cold tap water, soaked in a 20% Javex solution for 24 hours (to sterilize) and rinsed five times with filtered (0.22 M) double

Figure 35. Leaching apparatus.



deionized water. A 5 mL sample of the final rinse water was filtered through a sterile Nuclepore polycarbonate membrane to obtain a direct bacteria count according to the method described in Chapter 3. If no contamination was observed, the apparatus was packed with finely ground experimental material (Table 26) and the passage of sterile, deionized water from the jerrican was started. Five replicates of the apparatus shown in Figure 35 were used for each experiment so that all data reported represent the average of five observations from five independent sub-experiments.

The columns in Experiments 0 and 1 were sterilized by autoclaving at 121°C for one hour. In Experiments 4 and 8, the columns were sterilized by soaking the columns in a 10 g/L solution of sodium azide for 48 hours. Previous attempts to sterilize the columns with H_2S gas proved to be ineffective. All sterilized columns were tested for non-viability by culturing on brain-heart infusion agar at room temperature according to the method described in Chapter 3. Each litre of water which leached through the column was collected separately for analysis. In Experiments 0 to 4 the samples were analyzed for bacteria, tannins and lignins, carbohydrates, humic and fulvic acids, and dissolved organic matter. In Experiments 5 to 9 the samples were analyzed for bacteria, hardness, sulphate, iron, calcium, dissolved organic matter, oxygen, alkalinity, sodium, phosphate, manganese, cobalt, and copper. Sample size for the direct counts was determined by the desirability to observe 20 to 100 cells per field under the microscope (Jones and Simon 1975). Samples ranging from 1 to 5 mL of water were usually suitable. Dissolved oxygen was measured using the azide modification of the Winkler method (APHA 1975). The alkalinity of the samples was determined by the potentiometric titration method and the hardness by EDTA titration (APHA 1975). Sulphate was measured using the turbidometric method (APHA 1975). All of the metals including sodium were measured using a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer after acidifcation to pH 2 with 1:1 HNO_3. The organic constituents were analyzed according to the methods set out in Chapter 2. The pH of the samples was measured with a Sargent-Welch Model PBX meter equipped with a combination electrode.

Table 26. Geologic materials used in leaching experiments.

Experiment	Contents of Column	Wt.(g)
0 Cleach 1. Wab-Autoclaved	Wabamun Coal	130
1 Cleach 3. Can-Autoclaved	Canmore Coal	130
2 Cleach 4. Can-Unsterilized	Canmore Coal	130
3 Cleach 5. Wab-Unsterilized	Wabamun Coal	130
4 Cleach 6. Can-Sterilized-NaN_3	Canmore Coal	130
5 Cleach 8. Wab-Unsterilized	75% Wabamun Overburden 25% Wabamun Coal	150 50
6 Cleach 9. Wab-Unsterilized	90% Wabamun Overburden 10% Wabamun Coal	180 20
7 Cleach 10. Wab-Unsterilized	Revert Wabamun Coal Wabamun Overburden	1 3.6 175.4
8 Cleach 11. Wab-Unsterilized NaN_3	Wabamun Coal	130
9 Cleach 12. Wab-Unsterilized	Wabamun Overburden	190

4.2 RESULTS - THE ORGANIC CHEMISTRY OF COAL

4.2.1 Sterile Experiments

The concentration of all organic parameters measured declined in successive litres of leachate collected from sterilized coal from both sites, as might be expected. In contrast, the concentration of organic compounds showed a strong tendency to increase with leaching time, as shown in Figure 36, for Canmore coal treated with sodium azide. This trend was also observed for Canmore coal which had been autoclaved and for both treatments applied to Wabamun coal. Many bacteria were observed in all of the sterile leachate sampled by direct observation but attempts to culture them failed, confirming that they were dead. These bacteria leached out along with dissolved constituents and also showed a positive correlation with leaching time (Figure 36). Leachates from the autoclaved Canmore coal columns also showed a positive correlation between the numbers of (dead) bacteria and the concentrations of carbohydrates and fulvic acid (Figure 37). This may have been caused by the lysing of bacterial cells after death. The analytical problems associated with the measurement of fulvic acid do not preclude the possibility that other simpler organic compounds which could be released from cellular material are included in these analyses. Autoclaved Wabamun coal also showed significant correlations ($r > 0.9$) between (dead) bacteria in the leachate samples and tannins and lignins and carbohydrates. This effect was not observed with either type of coal treated with azide, suggesting that heat treatment may be modifying the organic chemistry of coal. For this reason, no particular significance can be attached to these results.

A summary of the total amount leached from the columns in Experiments 0 through 4 is reported in Table 27. Experiments 1 and 4, which were carried out with Canmore coal autoclaved and sterilized with sodium azide respectively, showed the lowest numbers of bacteria leached out. Experiments 2 and 3, which contain unsterilized Canmore coal and unsterilized Wabamun coal, contained higher numbers of bacteria suggesting that growth was occurring in the columns. These bacteria appeared to be free floating and were

Table 27. Summary of total amount leached for leaching experiments 0 to 4. Results are expressed in log form for bacteria, hours for leaching time, and g/g of material leached for the rest.

Expt. #	Log Bacteria	Leaching Time	Tannins and Lignins	Carbo-hydrates	Humic Acid	Fulvic Acid	Dissolved Organic Matter
0	5.98	---	3.9	7.7	11.5	50.0	69.2
1	4.52	229	.06	4.3	9.2	29.2	42.9
2	4.81	273	1.1	3.5	1.0	5.2	10.2
3	5.70	69	5.5	4.3	1.0	47.9	54.6
4	4.92	310	2.5	0	0.2	3.1	4.7

Figure 36. Canmore coal treated with sodium azide; relationships between organic parameters and leaching time.

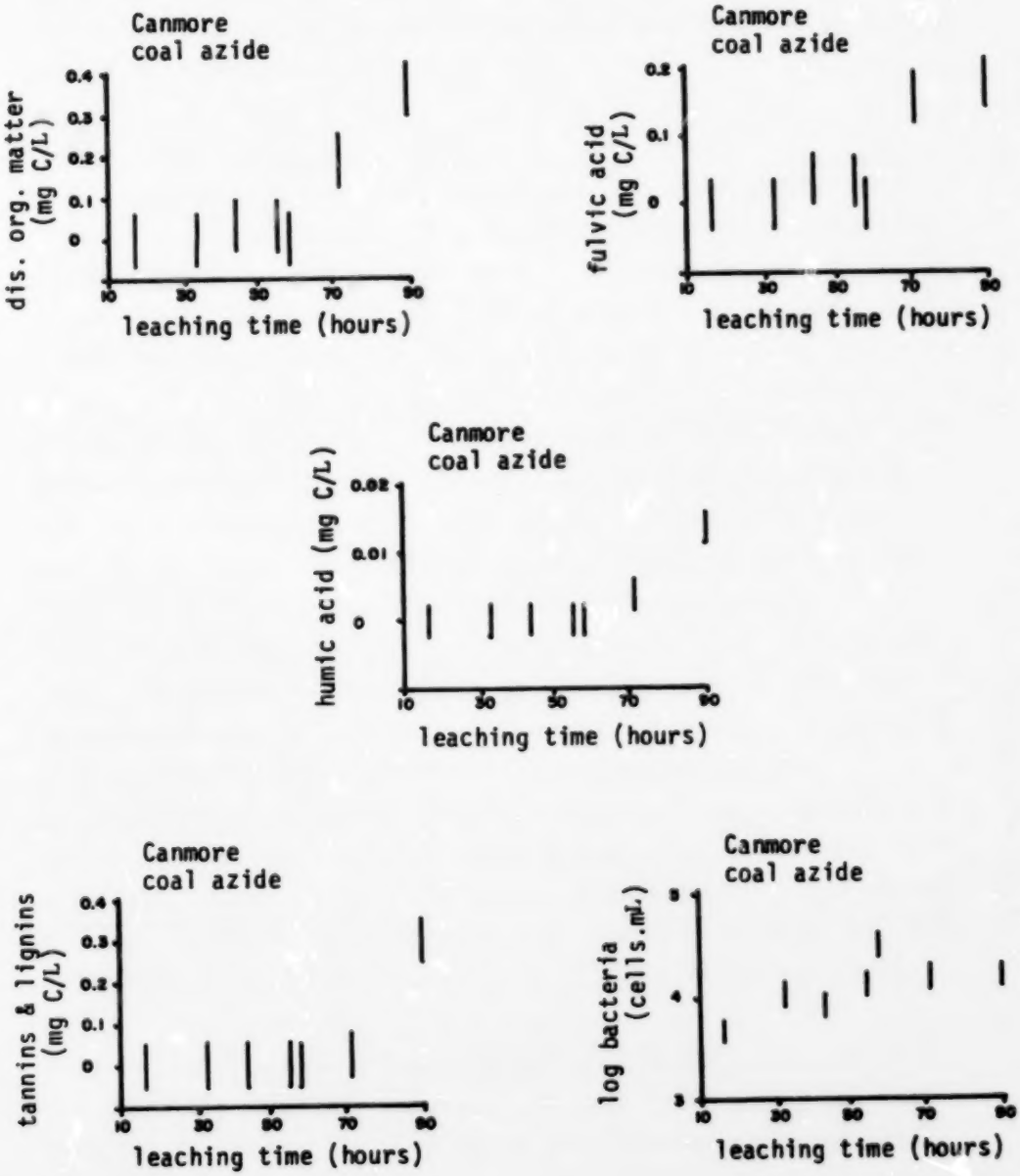
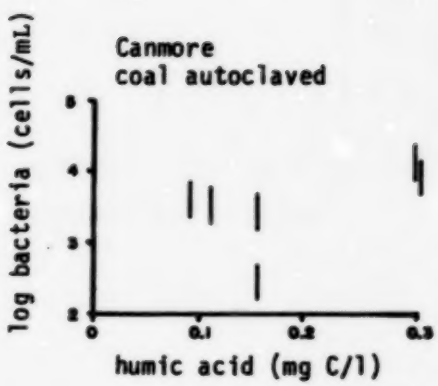
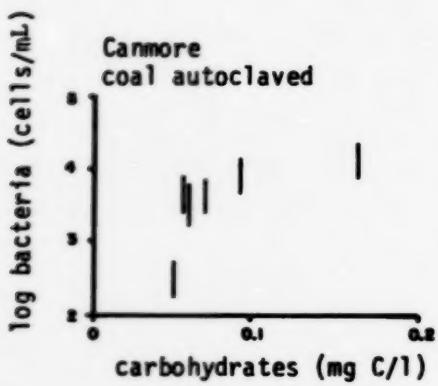
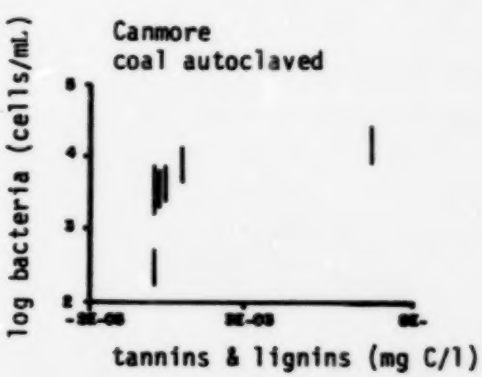
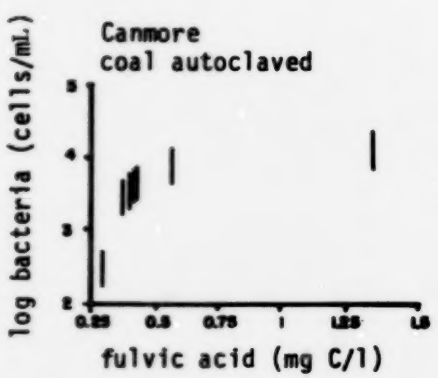


Figure 37. Autoclaved Canmore coal; relationships between bacteria and dissolved organic compounds.









easily leached out (plate culturing was used to confirm their viability) but no information is available on the numbers of bacteria which might be attached to coal particles and therefore immobile. In general, more organic matter could be leached from Wabamun coal, especially from autoclaved Wabamun coal. Canmore coal was more hydrophobic as shown by the much longer leaching times and yielded lower amounts of dissolved organic compounds. Unfortunately the facilities for inorganic analysis were not available for this first series of experiments.

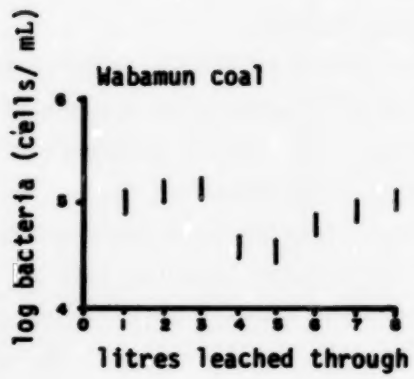
4.2.2 Non-Sterile Experiments

As with the sterile experiments, organic constituents decreased in concentration with successive volumes of leachate collected indicating that soluble organic compounds are easily mobilized in small quantities from ground up coal. In contrast with the sterilized coal, the concentration of organic parameters is not significantly related with either leaching time or bacterial populations. This situation is the same as that encountered under field conditions, presumably for the same reasons. The uptake of organic compounds by bacteria, especially labile molecules of carbohydrates and tannins and lignins, eliminates the control of leaching time upon concentration. The population of bacteria observed in the leachates declined at first with successive leaching volumes but later rose significantly suggesting that population growth was occurring (Figure 38). This occured most clearly in the Canmore coal columns but the subsequent rise in populations after the initial decline in the Wabamun columns suggests the same thing. A growth in population only occurs some time after an increase in food substrate, rendering the relationship between bacteria and concentration of organic compounds obscure. Nutrients may also be limiting.

4.3 THE LEACHING OF UNCONTAMINATED OVERBURDEN

This material, which did not need to be ground up, was very easily leached. All of the organic and inorganic parameters measured in the leachate declined very quickly in concentration with successive leaching volumes (Figure 39). In addition, the leaching

Figure 38. Unsterilized coal from Canmore and Wabamun; relationships between bacterial populations and successive volumes of leachate.



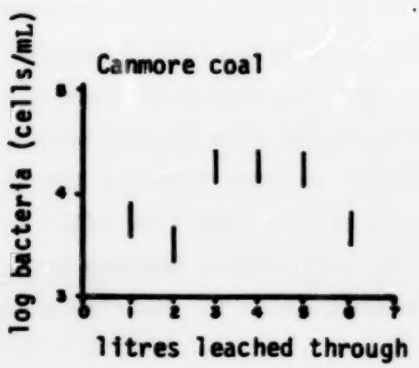
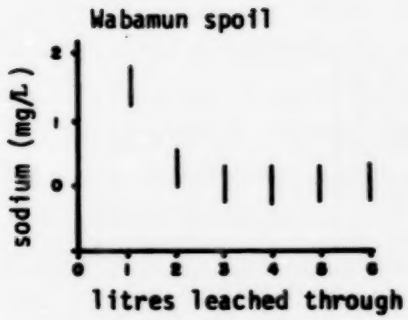
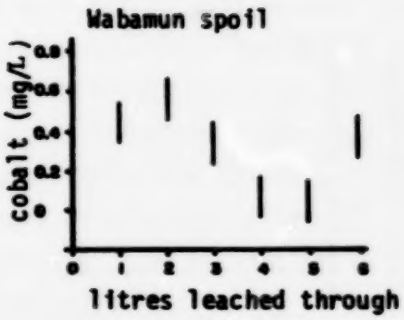
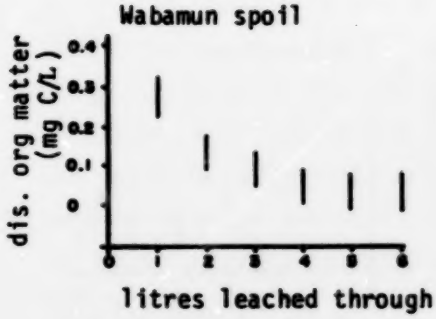


Figure 39. Wabamun overburden (spoil) material; relationships between various chemical parameters and successive leaching volumes.







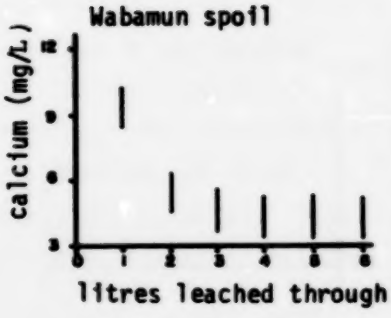
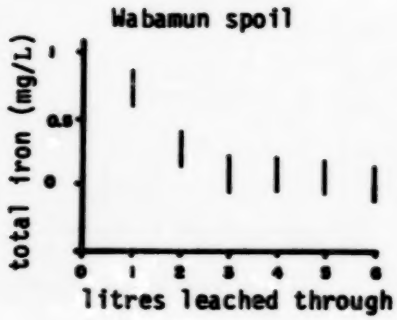
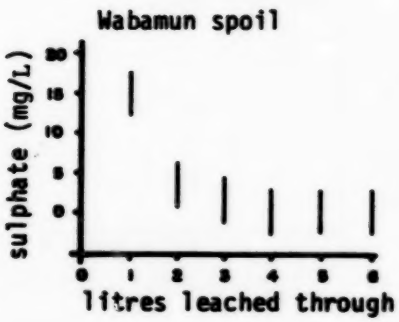
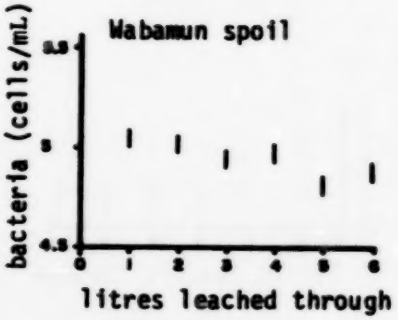
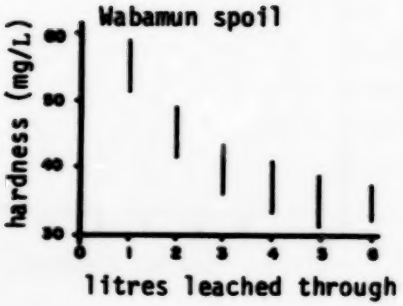


Figure 39. Concluded.









time did not affect the concentration of any parameter measured. A number of other significant ($r > 0.9$) correlations were found between various parameters measured in the leachate, however, which are summarized in Table 28.

These correlations may be broken down into three groups; those parameters associated with bacteria, those associated with dissolved organic matter, and the relationship between sodium and calcium. The correlations between bacteria, hardness, dissolved organic matter, and alkalinity are shown in Figure 40. The total amounts of all chemical and biological parameters leached from the overburden material are also shown in Table 29 under Experiment number 9. From this table, it can be seen that appreciable amounts of dissolved organic matter (28 µg/g) may be leached from overburden material in the absence of coal. The number of living bacteria which may also be leached out are significantly associated with hardness, alkalinity, and dissolved organic matter. The relationship with alkalinity is most probably related to the dissolution of carbon dioxide and to the dissolution of calcite. The pH was observed to rise from 7.0 to 8.1 in successive leaching volumes, supporting this hypothesis. The association with calcium is not surprising under these conditions. The relationship between bacteria and dissolved organic matter ($r = 0.90$) is of interest as it will be recalled that this only occurred rarely in the field and not at all (at least with the measure of total dissolved organic matter) in the pure coal columns. In Section 3.4, it was suggested that this relationship is usually obscured under stable, equilibrium conditions but that it was observed occasionally. The conditions in the leaching columns are not in equilibrium, however, as large amounts of water are being added to previously dry material. This correlation cannot be considered to be conclusive by itself but the data are suggestive.

Dissolved organic matter is significantly correlated with alkalinity, calcium, and sodium concentrations (Table 28 and Figure 41). The relationship with alkalinity and calcium is undoubtably tied in with the associations of these parameters with bacteria as discussed above. The mineralization of dissolved

Table 28. Statistical correlations between different parameters in the Wabamun overburden leaching experiment (#9).

X	Y	Regression Coefficient (r)
Hardness	Log Bacteria	.95
Dissolved Organic Matter	Log Bacteria	.90
Alkalinity	Log Bacteria	.94
Calcium	Sodium	.98
Alkalinity	Dissolved Organic Matter	.95
Calcium	Dissolved Organic Matter	.98
Sodium	Dissolved Organic Matter	.97

Table 29 Summary of total amount leached for leaching experiments 5 to 9. Results are expressed in log form for bacteria, hours for leaching time, and g of material leached for the rest. Iron is total iron as measured by atomic absorption spectrophotometry. DOM stands for Dissolved Organic Matter.

Expt.#	Log Bacteria	Leach. Time	Hard-ness	SO	Fe	Ca	DOM	O	Alka-linity	Na	PO	Co	pH	Terminal % Coal
5	6.23	59.8	1615	103	1.5	198	32	278	515	20	0	0	6.7	25
6	6.47	95	1284	100	1.9	295	44	295	705	17	0	0	6.6	10
7	6.82	312	2068	101	0	499	392	282	886	8	0	0	6.4	2 + Revert
8	6.03	245	--	--	0	--	17	374	755	309*	0	0	5.7	100
9	6.31	93	749	116	5.1	111	15.6	324	491	145	0	0	8.1	0

* High sodium value caused by the addition of sodium azide. Other measurements which are missing were caused by analytical difficulties.

Figure 40. Leaching of overburden; microbiological relationships.

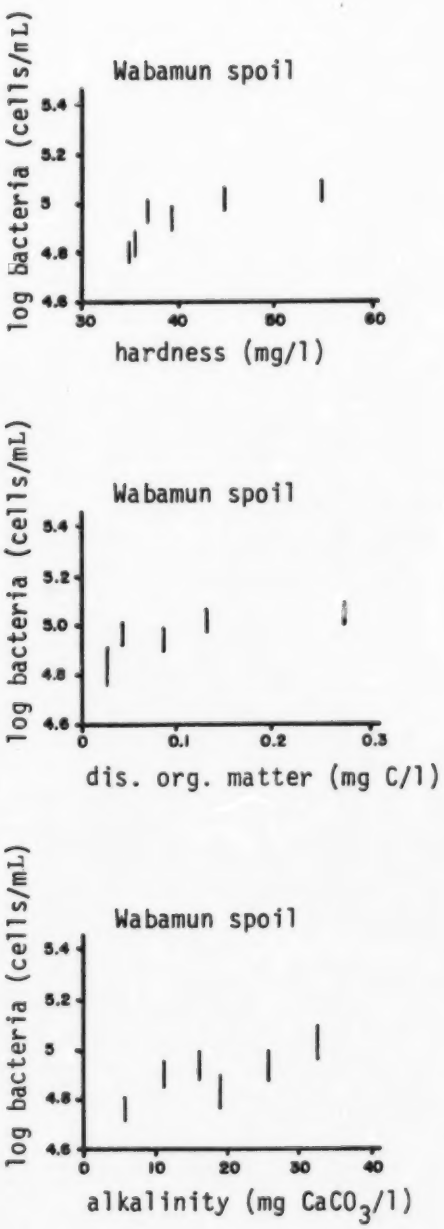
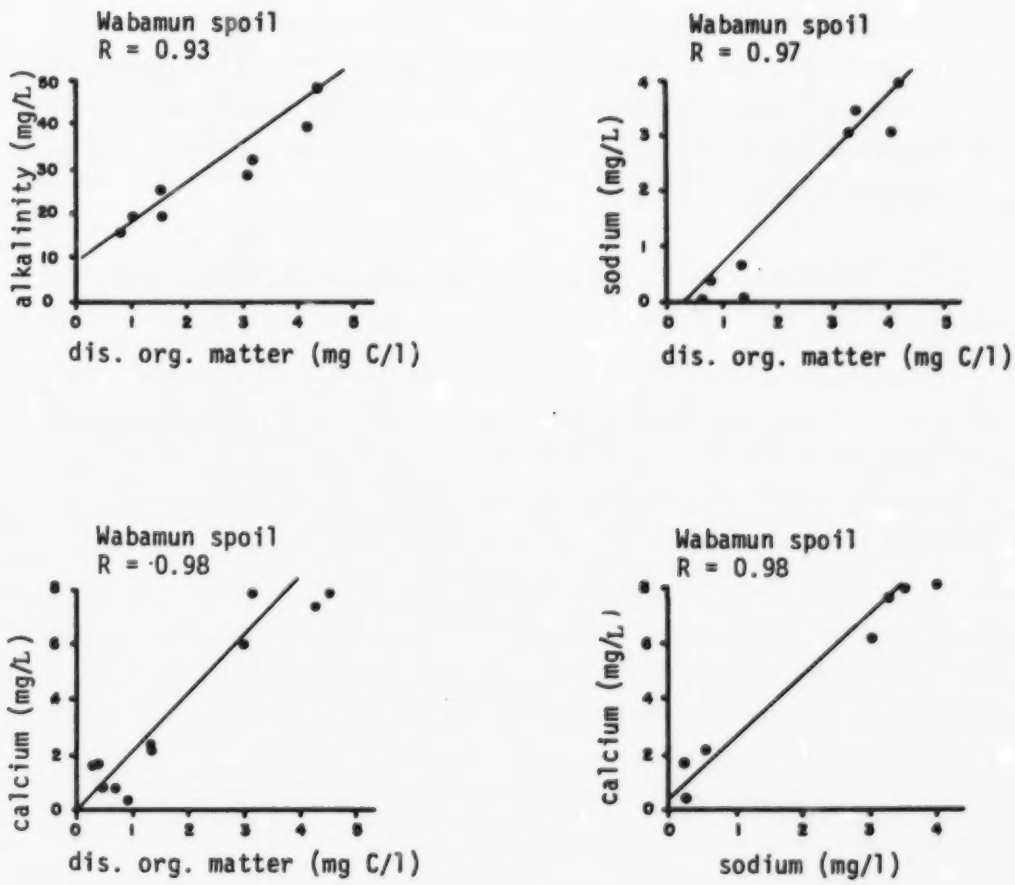


Figure 41. Leaching of overburden; inorganic relationships.



organic matter and the enhanced dissolution of minerals are known to be related, especially with regard to pH and Eh controls (Garrels and Christ 1965) but the effect of other thermodynamic considerations are difficult to separate without more detailed work. For the purposes of this discussion it is important only that they are related.

The fact that sodium and calcium are closely associated ($r = 0.98$) most probably relates to the clay content of the overburden material (Figure 41). Sodium and calcium are both closely associated with the dissolved organic matter content as well, indicating that an overall relationship may exist. This was also found to be the case when organic matter in the form of Revert was added to bentonite (Section 2.3), although the mechanism of such an interaction is not clear.

4.4 INFLUENCE OF VARYING AMOUNTS OF COAL IN OVERBURDEN MATERIAL ON THE CHEMISTRY OF LEACHATES

Experiments 5, 6, and 9 contained 25, 10, and 0% coal, respectively, mixed with overburden material and the resulting amounts of chemicals leached out are reported in Table 29 and Figure 42. Experiments 6 and 9 were repeated with good reproducibility so a fair degree of confidence may be placed in these data. From these, it can be seen that the amount of coal can affect aqueous overburden geochemistry. The results from Experiment 7, which included 2% coal and 0.6% Revert, are also reported in Table 29 and Figure 42 for comparative purposes. These latter results will be discussed in the next section in more detail.

From Figure 42 it may be seen that the amounts of leachable cations increased with increasing coal content except for iron. Alkalinity did not change significantly but the terminal pH dropped from 8.1 from pure overburden to 6.5 with 10% coal and remains at 6.6 with 25% coal. Dissolved organic matter increases with increasing coal concentration although the bacteria count did not show any clear trend with coal content. The leachable sulphate dropped by about 13% from 0% coal to 10% coal and remained at that level. The drop in pH is considered to be most significant in the light of increasing concentration of organic matter, as it suggests

Figure 42. Amounts leached from overburden containing varying amounts of organic matter.

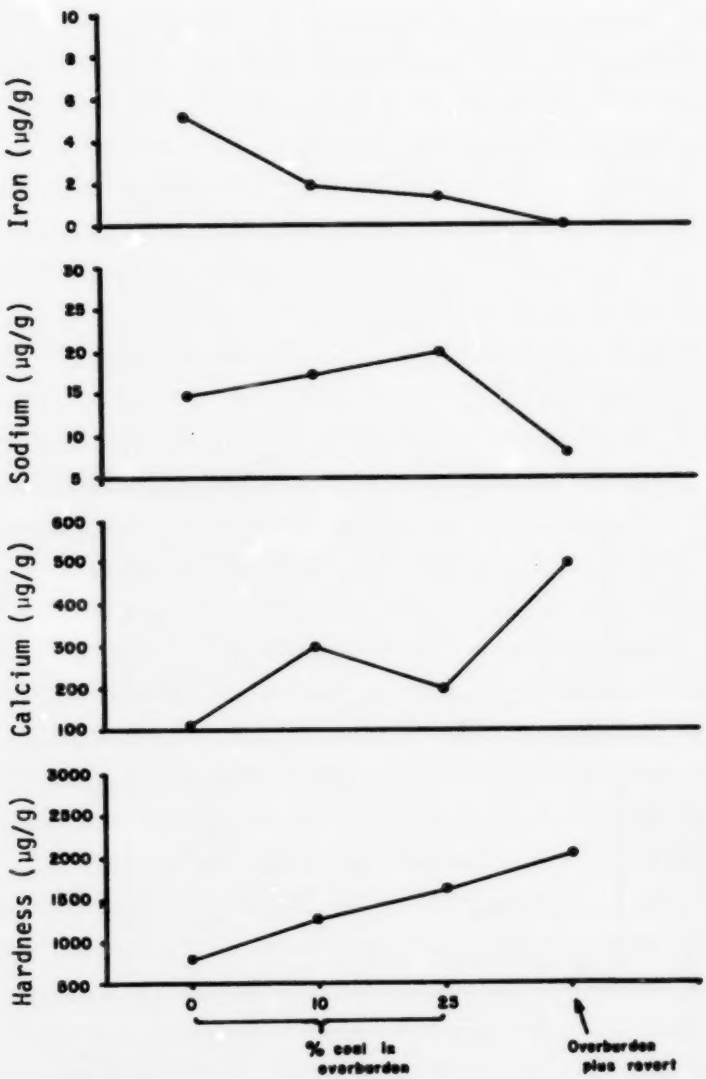
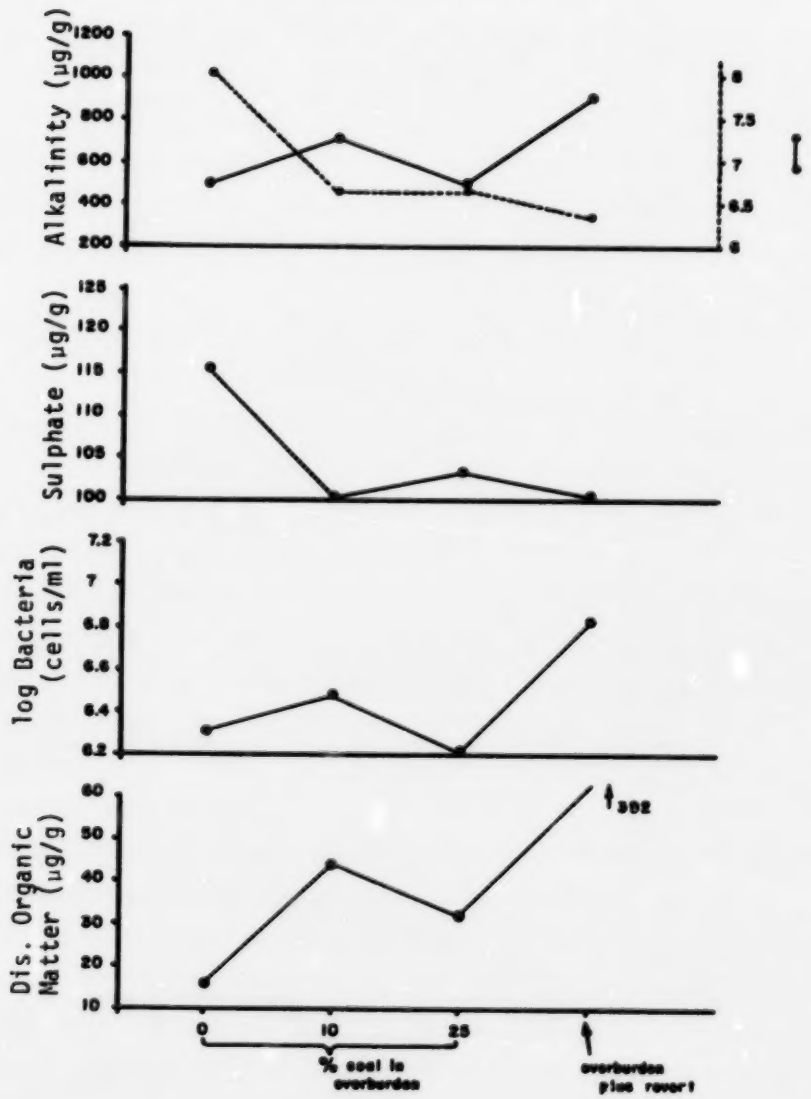


Figure 42. Concluded.



that organic matter was being mineralized to CO_2 and reacting with water to form carbonic acid. Hydrogen ion released from the dissociation of carbonic acid can react in turn with calcium carbonate and dolomite to release further bicarbonate ion and increase the concentration of divalent cations. This in turn might be expected to affect the cation exchange capacity of the clays present and increase the sodium concentration slightly as observed. The decrease in iron and sulphate are somewhat harder to understand. Iron may be influenced by the increases in dissolved organic matter by a chelation process or it may be a function of increased microbial activity. Sulphate may also be related to bacteria as it can function as a nutrient. In both cases, the decrease in concentration is small. These experiments were carried out aerobically so that sulphate reduction is improbable although some precipitation of iron as ferric hydroxide may be taking place.

4.5 THE INFLUENCE OF REVERT UPON THE CHEMISTRY OF LEACHATES

In all cases, except that of sodium, Revert seems to accentuate the effects discussed in Section 4.4. The presence of a labile organic substrate in the overburden boosted the dissolved organic matter concentration and the alkalinity of the leachates with a further drop in pH (Figure 42). The numbers of bacteria leached out were higher in this experiment than for any other (Table 29). Only 1 g of Revert was added to each overburden column and the average amount of dissolved organic matter leached out was 392 g/g of overburden or 70.6 mg from all of the spoil material measured as carbon. The average conversion factor for carbohydrates expressed as carbon to average molecular weight is 2.5, so approximately 177 mg of Revert was dissolved and leached out. The remaining 823 mg was either respired or left behind in the column. Visual observation confirmed that Revert was still present in the columns in reasonable quantities at the termination of the experiment suggesting that the degradation of the mud was not rapid and that time on the order of at least weeks would be required to degrade most of it under aerobic conditions at 5°C. Under anaerobic conditions, it would probably take even longer. The data collected by Groundwater Branch at the Whitewood Mine (Anon. 1979) suggest

that organic concentrations do not return to normal for several months, even with repeated pumping, bearing out this time estimate.

The behaviour of divalent cations, dissolved organic matter, bacteria, and alkalinity support the hypothesis put forward in Section 4.4 regarding the influence of mineralization of organic matter upon carbonate minerals. Sodium, however, does not behave in the same manner when Revert is present, as it did in the clay experiments described in Section 2.3. In these experiments, Revert seemed to catalyze the exchange of calcium for sodium on driller's bentonite resulting in very low calcium concentrations and high sodium. This was not observed in Experiment 7 suggesting that either the hypothesis is false or that native clays in low quantities do not behave in the same manner as driller's bentonite. While the former may be true, it is difficult to invalidate the results of Section 2.3 on the basis of Experiment 7 because of the different types and quantities of material involved. In the Revert-clay experiments, a large quantity of Revert and bentonite was added to a small amount of dissolved calcium and sodium. In Experiment 7, much more Revert (2 g/400 mL) and calcium (in both dissolved and mineral form) were present. In addition, the native clays cannot be assumed to be identical to driller's bentonite. On the basis of these results, it can only be said that the behaviour of Revert and driller's bentonite in the field can be duplicated in the laboratory but that native clays behave differently in controlled experiments. If bentonite plugs had not been used at Wabamun to seal the slotted portion of the casing, different cation results might have been found in the first few months after drilling.

4.6 DISCUSSION

The leaching experiments conducted with pure ground up coal demonstrate that Wabamun coal contains more soluble organic matter than does Canmore coal. Approximately 38% more dissolved organic matter could be leached from the former under sterile conditions (Table 27). When live bacteria were present, less dissolved organic matter was leached out in both cases and evidence of microbial growth in the columns was observed. Under sterile conditions, the

amount of organic matter leached out was closely related to the leaching time but this was not the case in the presence of live bacteria. Interestingly, humic acid was the most strongly depleted fraction suggesting that this class of compounds is more labile than previously suspected in both types of coal. The amount of dissolved organic matter which could be leached from overburden material in the absence of coal was only 29% of that leached from pure Wabamun coal, showing that coal can account for considerably more organic matter in solution than overburden on an equivalent weight basis. This was borne out by the experiments which tested various proportions of coal mixed with overburden material (Table 29) in which dissolved organic matter increased with increasing coal content (Figure 42). It is therefore concluded that coal leachate, either by itself or mixed with overburden, contains sufficient labile dissolved organic matter to support a large population of bacteria (which are intimately associated with it under natural conditions).

Increasingly, the amount of coal in the cast overburden serves to promote bacterial growth. The mineralization of the soluble organic matter releases CO_2 into solution which increases the alkalinity and lowers pH. The action of hydrogen ion on carbonate minerals further increases the alkalinity and also releases divalent cations, making groundwaters harder. The changes in divalent cation chemistry also influence sodium concentrations because of the clay present in the overburden. If more labile organic material, such as Revert, is present, these effects are accentuated. These experiments have shown that the presence of 10% coal in the cast overburden can boost alkalinity by 44%, hardness by 71%, and sodium by 17% (calculated from Table 29). The increase in hardness seems to be mostly from calcium, presumably from calcite. The small decrease in sulphate observed suggests that gypsum is not contributing very much calcium but gypsum precipitation may be occurring.

5. SYNTHESIS

Both the organic chemicals dissolved in unpolluted groundwaters and the organic matter found in coal have a common origin -- the degradation of terrestrial vegetation. The formation of coal took place millions of years ago but the same processes of decomposition may be observed today. In both cases, groundwater played an important role in transporting organic matter and defining the chemical and biological environment. In dealing with the organic geochemistry of groundwater, therefore, it is difficult to separate compounds originating from modern decomposition from those leached from coal. Normally, the two sources of organic matter are separated by varying thicknesses of overburden, as most terrestrial decomposition of vegetation takes place in shallow soil horizons. When strip mining of the coal occurs, however, organic matter from both sources is mixed indiscriminantly throughout the cast overburden under aerobic conditions. Microbial populations which are normally most abundant in shallow soil are also freely mixed, effectively inoculating the spoil material with bacteria and fungi which might not normally be found in deeper horizons. If groundwater re-invades the spoil material, its geochemistry may be expected to change because of chemical and physical weathering of the disturbed overburden. Groundwater evolution has traditionally been studied within the context of these processes. This study, however, is concerned with the possible effects of organic matter and micro-organisms on both the organic and inorganic geochemistry of mine spoil groundwaters.

The two reclamation sites studied, at Canmore and at Wabamun, are in two quite different areas geographically but they are not dissimilar geologically. Both places are rich in carbonate minerals and silaceous clastic rocks. Vegetation cover was boreal forest in both cases although shrubs and grassland are more common in the Wabamun area. The main difference between the two areas is the type of coal which was mined. Both may be classed as bituminous but Canmore coal is a higher grade (almost semi-anthracite in places) and Wabamun coal is sub-bituminous C. Measurements of oxygen content, pH, Eh, and temperature at both sites failed to reveal any major differences between the two sites and the organic

geochemistry was also quite similar. The proportions of the organic compounds found at Canmore and Wabamun were very comparable but more organic material dissolved in groundwaters was consistently found at the latter. This was shown to be directly related to the type of coal present in the spoil material. Concentrations of dissolved organic compounds were found to vary seasonally in both spoil and undisturbed material but the patterns observed were not perfectly synchronous. Low concentrations were found in the spring or early summer at both sites but seasonal peaks occurred throughout the year.

Samples taken from deeper installations tended to be lower in concentration within installation nests but no obvious general trend could be found with depth at either site. The path of groundwater movement was clearly identified at both sites and groundwater tended to decrease in concentration with respect to organic matter as it traversed both reclamation sites. Concentrations were often, but not always, lower in the undisturbed material compared with the spoil. The two most obvious influences on concentration were the length of time organic matter was exposed to degradation processes in the ground and the spring melt. Although the latter might have been expected to simply dilute organic matter already present in groundwater, as is often the case with inorganic constituents, the effects of the spring melt are more subtle than this. Previous work has suggested (Wallis et al. in press) that infiltrating precipitation is in fact rather concentrated with respect to organic matter because it tends to pick up easily dissolved materials which have accumulated during dry spells from biological activity. Samples of unsaturated soil zone water usually contain about an order of magnitude more organic matter in solution when sampled from soil horizons. Spoil material which has been reclaimed would, of course, have a much less well developed soil layer but both of these sites were covered with grasses or alfalfa and some input from decaying vegetation would be expected. Increased water movement might also be expected to pick up more soluble organic material leached from coal which has been left behind in the spoil. A seasonal peak in concentration might therefore be expected from the influence of the spring melt and this was sometimes observed.

Organic matter, however, is not conservative in groundwater. It serves as a nutrient source for large populations of heterotrophic bacteria in both shallow and deep horizons. The influx of spring meltwaters mobilizes this organic matter as well as other inorganic nutrients which accumulate from decomposition in drier spells. The result is a large increase in heterotrophic activity which continues until something becomes limiting. This may be the concentration of organic matter or it might be that of other nutrients such as phosphate or nitrate (always in short supply under natural conditions). Assuming that inorganic nutrients do not become limiting right away, the rapid increase in biological degradation which takes place in the spring could result in a slug of organically deficient water which eventually reaches the groundwater table sometime later in the year. As groundwater chemistry tends to become averaged because of differential rates and amounts of chemical inputs over large areas, a seasonal dilution effect may easily become obscured or delayed. For these reasons it is difficult to relate an increase in hydraulic head measured during the spring melt to lowered concentrations of dissolved organic matter.

Because the organic matter in groundwater is not conservative, older waters which have been in contact with microorganisms for some time are usually lower in concentration. As older groundwaters are usually found in deeper formations, the decrease in concentration with depth is to be expected. Similarly, groundwaters which are flowing out of a reclamation site have been exposed to microbial communities for a longer time than recently infiltrated water in shallow horizons or deeper groundwaters flowing into the spoil pile from upstream. This, presumably, accounts for the decrease in concentration as groundwater traverses the reclamation site.

Bacteria are the most important organisms found in groundwater. Many different types are present, both heterotrophic and autotrophic. The former are well adapted to utilizing the organic matter present in low concentrations. As plant material is degraded, the simpler compounds are rapidly mineralized or broken down to simpler compounds. These can re-combine and be further broken

down by physiologically different groups of bacteria. More complex compounds are degraded slowly and their by-products are also available for chemical aggregation reactions. The breakdown of these more resistant chemicals often takes many different steps and may involve several groups of bacteria. The aggregation reactions which occur result in the production of large molecular weight humic compounds which are chemically heterogeneous and resistent to microbial attack. It is for this reason that most of the organic material dissolved in natural waters is humic in nature. It is difficult to observe an obvious correlation between bacterial populations and the concentration of dissolved organic matter because of the differential rates of degradation which occur and because the majority of organic material being measured is not being rapidly decomposed. If more labile material suddenly becomes available, bacterial populations will expand and species composition may shift until either the material is used up or some other nutrient becomes limiting. Unless samples are taken at such a time and processed very quickly, it is doubtful that any relationship would be observed. If such a relationship is found, and it was occasionally throughout the course of this study, it may be interpreted as evidence for a change in the loading rate or composition of organic matter. Ordinarily, however, the relationship between bacteria and organic matter is one of dynamic equilibrium characterized by a relatively stable concentration and composition of dissolved organic matter and slowly fluctuating populations of bacteria.

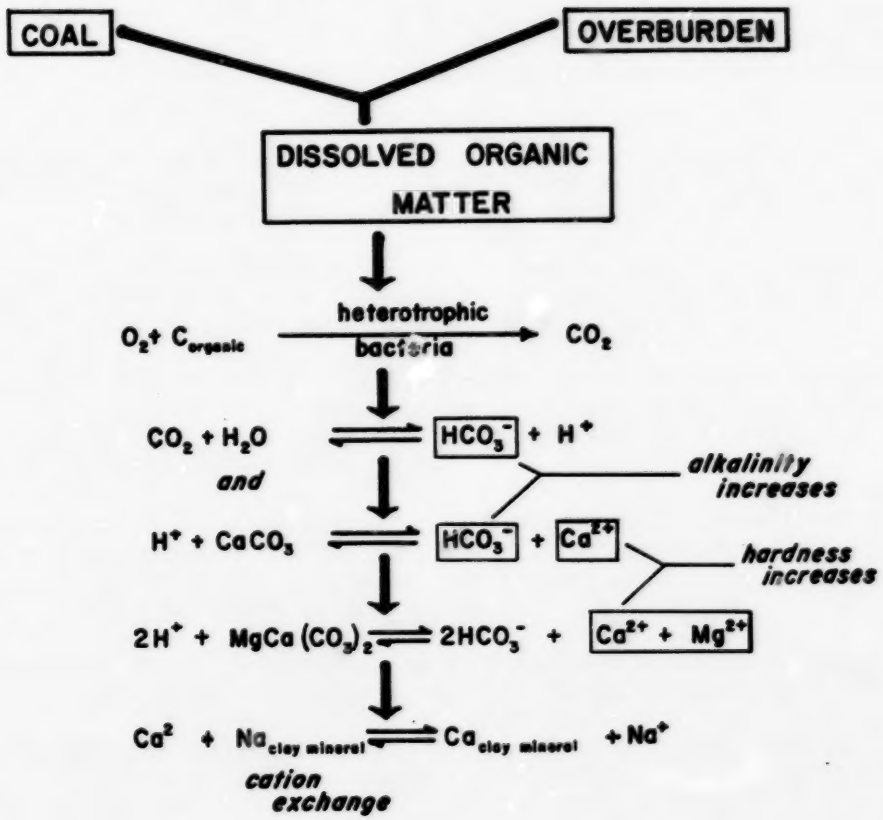
Autotrophic bacteria influence the inorganic chemistry of groundwater mainly through the activities of sulphur and iron bacteria. Depending upon the amount of oxygen present, sulphide minerals may be oxidized to sulphate or sulphate may be reduced to hydrogen sulphide or back to mineral sulphides. Evidence for both activities was found during this study although it is not possible to assess the importance of these processes quantitively. Certainly, the reduction of sulphate by sulphur reducing bacteria has imparted a nasty odour and taste to groundwaters at some sites such as P6 at Canmore and Site 4 at Wabamun. Unfortunately, it was not possible to investigate the activities of iron bacteria because of

methodological difficulties but they are known to be present at Canmore at least in surface waters. The high concentrations of iron at some sites at Wabamun strongly suggest the presence of this group of bacteria there as well. It is possible that pyrite minerals in the overburden are being oxidized by such organisms as Thiobacillus. This activity is responsible for acid mine drainage in the unbuffered waters of the eastern United States but has not yet been definitely proven in western Canada. Microbiologists in Montana, however, have isolated various species of Thiobacillus, including the infamous T. ferroxidans at the Decker coal mine site. Acidification problems in mine drainage waters are not known in the west because of the calcareous nature of the overburden there, but chemical neutralization by carbonate minerals also increases the hardness and alkalinity of groundwaters to an unknown extent.

The effect of increasing amounts of coal in overburden material has been investigated by this study by laboratory leaching experiments. The major effects identified were increases in alkalinity and hardness of groundwater caused by the mineralization of organic matter by bacteria. A conceptual model of this process is presented in Figure 43. Organic matter leached from coal, and to a certain extent the overburden itself, is mineralized by heterotrophic bacteria at varying rates into CO_2. The carbon dioxide produced dissolves and reacts with water to form carbonic acid which dissociates into hydrogen ion and bicarbonate ion. The acidity produced by this reaction is neutralized by carbonate minerals but more calcium, magnesium, and bicarbonate ions are released into solution. As a result, hardness and alkalinity both increase although the pH remains basic. The increase in concentration of divalent cations also appears to cause a certain amount of cation exchange with clay minerals, releasing some sodium.

It is difficult to separate the effects of chemical weathering caused by mechanical disturbance of overburden material from the effects of the process outlined above. The laboratory experiments described in this report indicate that hardness may increase by as much as 71% and alkalinity by 44% if 10% of the spoil material is coal. The actual amount of coal mixed with overburden

Figure 43. Effect of coal on inorganic geochemistry of overburden at Wabamun.



is probably much less than this on the average and more detailed field and laboratory work would be necessary to gain an estimate of the actual effect. This work is now underway by the Kananaskis Centre under separate contract at the Battle River site. It may be said, on the basis of this report, however, that hardness and alkalinity problems experienced with the reclamation of groundwater resources at strip mine sites are aggravated by increasing amounts of coal in the spoil material.

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